Universidade Nova de Lisboa
Faculdade de Ciências e Tecnologia

Safety Commission

Water treatments in semi-closed cooling circuits and their impact on the quality of effluents discharged by CERN

Mestrado em Gestão de Sistemas Ambientais

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Lisboa
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MESTRADO INTEGRADO EM ENGENHARIA DO AMBIENTE

Perfil: **Gestão de Sistemas Ambientais**

Dissertação orientada pela Professora Doutora
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Sumário

Este estudo tem como objectivo principal avaliar o impacto das descargas dos circuitos semi-fechados de refrigeração à água do CERN (European Center for Nuclear Research) na qualidade dos seus efluentes, tomando como guia a legislação internacional apoiada por um conhecimento dos sistemas de água do CERN.

Para tal, analisou-se o funcionamento do sistema semi-fechado de refrigeração por água dos aceleradores de partículas do CERN, bem como o tratamento das águas que é efectuado para prevenir proliferação de bactérias como, por exemplo, a *Legionella*.
Procedeu-se ainda à análise dos produtos utilizados no tratamento das águas do sistema semi-fechado de refrigeração dos aceleradores de partículas, bem como os eventuais impactos no ambiente provenientes do uso desses produtos.

Realizou-se também um levantamento da regulamentação aplicável aos efluentes do CERN, tanto da lei suíça e francesa (onde o CERN se encontra) como de algumas leis internacionais como a europeia, portuguesa, espanhola, alemã, norte americana e canadense com vista não só a uma melhor compreensão do significado dos valores limites da legislação dos estados membros do CERN, como também a um possível estabelecimento de um regulação interna do CERN com respeito as descargas de água.
Em seguida, efectuou-se uma pesquisa sobre os tipos de parâmetros a analisar tendo em conta a legislação aplicável, os produtos utilizados e as condições de descarga, compreendendo também uma discussão sobre alguns parâmetros mais problemáticos como por exemplo o AOX.

Partindo deste trabalho, realizaram-se quatro campanhas de amostragem de água no sistema semi-fechado de refrigeração do CERN, duas durante o tratamento de choque preventivo e duas campanhas durante o tratamento normal. O objectivo das duas primeiras campanhas foi mais abrangente uma vez que se pretendia verificar a conformidade das águas do CERN com a Lei dos estados membros; Por outro lado, as campanhas realizadas durante o tratamento normal foram orientadas para um melhor conhecimento de parâmetros mais problemáticos como AOX, COD, CQO, Cloro e Zinco. A preparação para estas campanhas incluiu também a escolha de outros aspectos como: os três pontos de analise (RAMSES, SF1 e edifício 863), o momento de amostragem e a selecção de um laboratório externo para as análises.

A análise de resultados mostrou que os efluentes do CERN no ponto de descarga (RAMSES) estão de acordo com a legislação. No entanto, na origem destes efluentes (os circuitos de SF1 e de edifício 863) surgiram algumas não conformidades. Os parâmetros AOX, COD, CQO, Cloro, Bromo, matéria em suspensão, Zinco e Alumínio verificaram ser os mais problemáticos.
Realizou-se ainda uma procura de métodos alternativos aos parâmetros convencionais para testar a qualidade da água compreendendo um estudo sobre a aplicabilidade de testes ecotoxicológicos. Após este estudo realizou-se uma campanha utilizando os testes Microtox (Vibrio fischeri), Algas verdes (Pseudokirchneriella subcapitata), Micro-crustáceos (Daphnia magna), Macrofitas (Lemma minor) tendo-se chegado a uma conclusão conducente a anterior. Assim, RAMSES não apresentou toxicidade nos quatro testes enquanto SF1 apresentou já alguma toxicidade, sendo mais sensível ao teste com Micro-crustáceos, onde apresentou UT_{50} de 7,1 e um EC_{50} de 14,2 %.

Abstract

The main goal of this study is to assess the impact of the discharges of the semi-closed water cooling circuits of CERN (European Center for Nuclear Research) on the overall quality of CERN's effluents, taking as guidelines the international legislation supported on the knowledge of the water systems of CERN.

In order to reach this goal, a thorough analysis of the functioning of the semi-closed water cooling systems of CERN's particle accelerators was done, as well as, an analysis of the treatment that is done to prevent the proliferation of bacteria such as *Legionella*.
The products used in these water treatments, as well as their impact, were also researched.

In addition, a study of the applicable regulation to CERN's effluent was done. This study considered not only the regulation of France and Switzerland (CERN's host states) but also the international regulation from the European community, Portugal Germany, Spain, U.S. and Canada, having in view a better understanding of the limit values of the parameters of the CERN's host states, as well as, the possibility of setting a CERN's internal regulation concerning water discharges.
Considering the applicable regulation, the products used and the discharge conditions of the water systems, a research on the types of parameters to analyse was undertaken, bearing in mind the controversy on parameters such as AOX.

This research was the foundation for conducting four water sampling campaigns: two of which during preventive shock treatment and the remaining two during regular treatment. The objective of the first two campaigns was broader and intended to check the conformity of CERN's effluents with the regulations of the host states; On the other hand, the sampling campaigns conducted during regular treatment were oriented to deepen the knowledge on problematical parameters such as AOX, COD, DOC, Chlorine and Zinc. The preparation for these campaigns included also the choice of other aspects such as: the three sampling points (RAMSES, SF1 and building 863), the definition of the schedule for sampling and the selection of an external laboratory to conduct the analyses.

The results of the analyses of CERN's effluents, at the discharge point (RAMSES), were fully compliant with the regulation. However, at the source of this effluents (circuits SF1 and building 863) non-conformities have surged. The parameters AOX, DOC, COD, Chlorine, Brome, Suspended matter, Zinc and Aluminium demonstrated to be the most problematic.

To conclude this work, a search for alternative methods to conventional water quality parameters was done that included a study on the applicability of ecotoxicological tests. As a result of this study, a final sampling campaign was performed using the tests Microtox (Vibrio fischeri), Green Algae (Pseudokirchneriella subcapitata), Micro-crustaceans (Daphnia magna), Macrophytes (Lemma minor) having obtained results that were conducive with the previous results. This way, RAMSES didn't not show any toxicity on the four tests whilst SF1 evidenced toxicity, being most sensitive to the Micro-crustaceans test where it presented a UT_{50} value of 7,1 and EC_{50} value of 14,2 %.

Résumé

Le principal objectif de cette étude est d'évaluer l'impact des décharges des circuits demi-fermés de refroidissement par l'eau du CERN (Centre Européen pour la Recherche Nucléaire) sur la qualité globale des effluents du CERN, prenant comme directives la législation internationale agrémentée par la connaissance des circuits de refroidissement du CERN.

Cet objectif ne pourrait pas être atteint sans une étude complète sur le fonctionnement des systèmes demi-fermés de refroidissements par l'eau des accelérateurs de particules du CERN. En parèlle, une analyse du traitement a été également faite afin d'empecher la prolifération de bactéries telles que la *Legionella*. Les produits utilisés dans ces traitements de l'eau, ainsi que leur impact, ont été également étudiés.

Par ailleurs, une étude du règlement applicable à l'effluent du CERN a été faite. Cette étude considérait non seulement le règlement de la France et de la Suisse (États de l'accueil du CERN) mais également le règlement international la Communauté européenne, du Portugal de l'Allemagne, de l'Espagne, des États-Unis et du Canada, ayant en vue un meilleur arrangement des valeurs limites des paramètres des États de l'accueil du CERN, ainsi que la possibilité de placer le règlement interne du CERN traitant le sujet de la décharge d'eau.

En considérant le règlement applicable, les produits employés et les conditions de décharge des circuits de refroidissement, une recherche sur les types de paramètres a analyser a été entreprise, prenant en compte la polémique sur des paramètres tels qu'AOX.

Cette recherche était la base qui a conduit à quatre campagnes de prélèvement de l'eau: deux pendant le traitement de choc préventif et deux autres pendant le traitement régulier. L'objectif des deux premières campagnes avait un caractère plus large et été prévu afin de pouvoir vérifier la conformité des effluents du CERN avec les règlements des États d'accueil ; D'autre part, les campagnes de prélèvement conduites pendant le traitement régulier ont été orientées pour approfondir la connaissance sur des paramètres problématiques tels qu'AOX, DCO, CQO, Chlore et Zinc. La préparation pour ces campagnes a inclus également le choix d'autres aspects tels que : les trois points de prélèvement (RAMSES, SF1 et bâtiment 863), la définition du programme pour le prélèvement et le choix d'un laboratoire externe pour réaliser les analyses.

Les résultats des analyses des effluents du CERN, au point de décharge (RAMSES), étaient entièrement conformes avec le règlement. Cependant, à la source de ces effluents (circuits SF1 et bâtiment 863), des non-conformités sont apparues. Les paramètres AOX, DOC, COD, Chlore, Brome, corps suspendus, Zinc et Aluminium se sont révélés être les plus problématiques.

Pour conclure ce travail, une recherche des méthodes alternatives aux paramètres conventionnels de qualité de l'eau a été réalisée, incluant une étude sur l'applicabilité des essais écotoxologiques. En raison de cette étude, une campagne finale de prélèvement a été exécutée utilisant les essais Microtox (Vibrio fischeri), algues vertes (Pseudokirchneriella subcapitata), Micro-crustacés (Daphnia Magna), macrophytes (Lemma mineur) dont les résultats obtenus correspondaient et vérifiaient les résultats précédemment obtenus. De cette façon, RAMSES n'a montré aucune toxicité sur les quatre essais tandis que SF1 démontrait la toxicité, étant plus sensible au test des Micro-crustacés présentant une valeur UT50 de 7.1 et la valeur EC50 de 14,2 %.

Resumen técnico

Este estudio tiene como objetivo principal evaluar el impacto de las descargas de los circuitos semi-cerrados de CERN (European Center for Nuclear Research) en la calidad de sus efluentes, tomando como guía la legislación internacional, apoyada por el conocimiento de los sistemas de agua de CERN.

Para esto, se analizó tanto el funcionamiento del sistema semi-cerrado de refrigeración por agua de los aceleradores de partículas de CERN como el tratamiento efectuado en las aguas para prevenir la proliferación de bacterias, como *Legionella.* Se analizaron también los productos utilizados en el tratamiento de las aguas del sistema semi-cerrado de refrigeración de los aceleradores de partículas, así como los eventuales impactos ambientales derivados del uso de esos productos.

Se realizó un estudio de la regulación aplicable a los efluentes de CERN, tanto de la Ley Suiza y Francesa (donde se encuentra ubicado CERN) como en algunas leyes internacionales como la Europea, Portuguesa, Española, Alemana, Norte-americana y Canadiense, con vista no sólo a una mejor comprensión del significado de los valores límites de la legislación de los estados miembros de CERN si no como también a un posible establecimiento de una regulación interna de CERN con respecto a las descargas de agua.

Seguidamente, se efectuó una investigación sobre los tipos de parámetros a analizar teniendo en cuenta la legislación aplicable, los productos utilizados y las condiciones de descarga, comprendiendo también una discusión sobre algunos de los parámetros más problemáticos, como por ejemplo AOX.

Partiendo de este trabajo, se llevaron a cabo cuatro campañas de muestreo de agua en el sistema semi-cerrado de refrigeración de CERN; dos campañas durante el tratamiento de choque preventivo y dos campañas durante el tratamiento habitual. El objetivo de las dos primeras campañas fue más general una vez se decidió verificar la conformidad de las aguas de CERN con la Ley de los Estados miembros. Por otro lado, las campañas realizadas durante el tratamiento normal fueron orientadas a obtener un mejor conocimiento de los parámetros más problematicos; AOX, COD, DQO, Cloro y Zinc. La preparación de estas campañas incluyó también la definicíon de otros aspectos como los tres puntos de muestreo (RAMSES, SF1, Edificio 863), el momento de muestreo y la selección de un laboratorio externo para los análisis.

El análisis de los resultados mostró que los efluentes de CERN en el punto de descarga (RAMSES) están de acuerdo a la legislación. Sin embargo, en el origen de estos efluentes (los cirucuitos de SF1 y del Edificio 863) surgieron algunas disconformidades. Los parámetros AOX, COD, DQO, Cloro, Bromo, Materia en Suspensión, Zinc y Aluminio fueron los más problemáticos.

También se realizó una búsqueda de métodos alternativos de los parámetros convencionales para testar la calidad del agua que comprendiera un estudio sobre la aplicabilidad de tests ecotoxicológicos. Después de este estudio se realizó una campaña utilizando los tests “Microtox” (*Vibrio fischeri*), “Algas verdes” (*Pseudokirchneriella subcapitata*), “Micro-crustáceos” (*Daphnia magna*), y “Macrófitas” (*Lemma minor*). Las conclusiones con estos tests fueron similares a los anteriores tests realizados: RAMSES no presentó toxicidad en los cuatro tests, SF1 presentó alguna toxicidad, siendo el más sensible el test con Micro-crustáceos, donde presentó un UT_{50} de 7,1 y un EC_{50} de 14,2 %.

List of Acronyms

AOX – Adsorbable Organic Halides;
BDO_5 – Biological Demand for Oxygen;
BSM – Beyond the Standard Model of particle physics;
BT – Benzotriazole;
CAS – Central Authentication Service;
CDO – Chemical Demand for Oxygen;
CERN – European Centre for Nuclear Research;
CIPEL – Commission internationale pour la protection des eaux du Léman contre la pollution, Lausanne;
COFRAC – Comité Français d'Accréditation;
DOC – Dissolved Organic Carbon < 0.45 μm;
EC – Effective Concentration of a sample that cause 20% (EC_{20}) or 50% (EC_{50}) inhibition in the luminescent bacteria test;
EPA – Environmental Protection Agency of the United States;
GL – Dilution level at which a wastewater sample causes less than 20% inhibition to the measured specie.
ISO – International Organization for Standardization;
LEP – Large Electron-Positron Collider;
LHC – Large Hadron Collider;
MSDS – Material Safety Data Sheet;
NPDES – National Pollutant Discharge Elimination System (U.S.);
PS – Proton Synchrotron;
RAMSES – The LHC RAdiation Monitoring System for the Environment and Safety;
RC – Ratio of the conductivity between the raw water and the water existing at the cooling circuits;
SC / IE – Safety Commission / Integrated Safety & Environment Group;
SETAC – Society of Environmental Toxicology and Chemistry;
SPS – Super Proton Synchrotron;
TOX – Total Organic Halides;
TRC – Total Residual Chlorine;
TS/CV – The Cooling and Ventilation Group of Technical Support Division;
TT – Tolyltriazole;
TU – Toxic Units;
UFC/m^3 – Units forming colonies per cubic meter;
WET – Whole Effluent Toxicity;

Index:

Index of Figure

Index of Tables

1. CONTEXT OF THIS STUDY

Along with the improvement of systems,
comes the necessity to adapt to those changes.

CERN's accelerators, as well as other CERN facilities, are cooled by several types of water systems. This study is focuses on the water cooling systems.

In order to reduce the consumption of water, CERN optimized the structure of the cooling circuits, turning its previously open water circuits into semi-closed cooling circuits which imply much less water consumption. This change has enabled CERN to cut its water consumption to less than a third, going from 20 million of cubic metres per year to 6 million of cubic metres per year. *[7]*

However, this reduction brought forward new problems, such as the new semi-closed water cooling circuits are more susceptible to proliferation of bacteria such as *Legionella*, due to the re-use of the water.

Simultaneously, *Legionella* issues have risen in the host states (both in France and Switzerland) which have lead to a re-enforcement of the regulations on this matter.

To face this situation, CERN recently increased the usage of chemical products in water treatments in order to master the *Legionella* growth in the circuits, ensuring, this way, the safety of personnel and the good functioning conditions of the cooling systems.

However, this action may change the quality of the periodic water discharges from the semi-closed cooling circuits, once the usage of these products just like the consumption of water, present also a possible environmental hazard that, as such, must be controlled.

2. OBJECTIVES OF THIS STUDY

The objectives of this study are the following:

- Gain a deeper knowledge of the water quality of effluents discharged by CERN's cooling circuits that are affected by the mentioned water treatments;
- Gain knowledge of the international situation in effluent water regulation having in view the creation of a CERN internal regulation;
- Understand possible hazards and assess the impact on receiving rivers;
- Check legal conformity of these effluents with the Swiss/French and EU regulations;
- Find alternative ways of controlling effluent water quality.

3. CERN – THE EUROPEAN CENTRE FOR NUCLEAR RESEARCH

This study has been conducted for and within CERN and it is therefore necessary to make a description of the organization in hand.

3.1 General Description

CERN, the European Centre for Nuclear Research, is the world's most advanced fundamental research institute for particle physics.

"*CERN is a laboratory where scientists unite to study the building blocks of matter and the forces that hold them together*" *– [Robert Aymar, Director General of CERN]*

CERN was created with the aim of providing scientists with the necessary tools for research. These tools are the accelerators which accelerate particles to almost the speed of light and the detectors that make those particles visible.

"The Organization shall provide for collaboration among European States in nuclear research of a pure scientific and fundamental character, and in research essentially related thereto. The Organization shall have no concern with work for military requirements and the results of its experimental and theoretical work shall be published or otherwise made generally available." - [CERN Convention]

Founded in 1954, the laboratory was one of Europe's first joint ventures, being a proof of peace and progress through scientific collaboration. Over the past 50 years, it has become a prime example of international collaboration and is currently supported by 20 European member states as shown in image I, having over 7000 visiting scientists and engineers from over 80 countries.

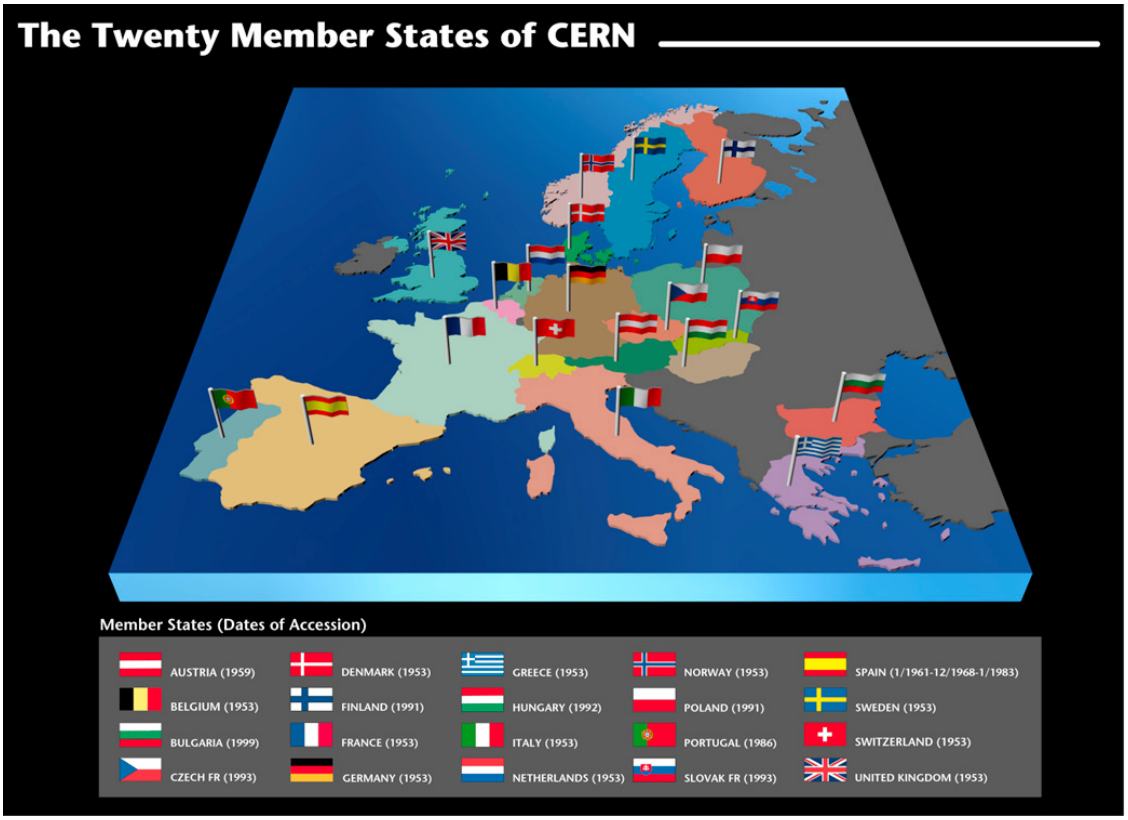


Figure I – Member states of CERN and their joining times

Since its creation CERN has not stopped progressing and now has an annual budget of about 1000 MCHF supporting more than 2400 highly qualified staff in cutting edge areas such as physics, computer science, electronics and electricity, mechanics and material science, cryogenics and ultrahigh vacuum, radiation protection, cooling and ventilation, operation of accelerators and associated equipment, conventional and superconducting magnets, radio-frequency.

3.2 A glimpse of the historical background

CERN was founded in the years following the Second World War, when the claim for an international collaboration gave birth to the United Nations with its agencies. Among the severe consequences of the war, Europe was facing the emigration of established scientists, attracted by the prestige of American laboratories.

In 1944, at the European Cultural Conference at Lausanne, the French physicist and Nobel prize-winner Louis de Broglie proposed the creation of a European science laboratory, with a view to restore European science to its former prestige. This suggestion was also discussed during two conferences of the UNESCO in 1952, and led to the creation of a provisional Council, the "Conseil Européen pour la Recherche Nucléaire" (CERN). At that time, pure physics research concentrated on understanding the inside of the atom, hence the word "nuclear". In 1953 the Council decided to build a central laboratory astride the Franco-Swiss border west of Geneva at the foot of the Jura Mountains.

At the time, the creation of the council was supported by twelve states, called Member States. The twelve founding Member States are: Federal Republic of Germany, Belgium, Denmark, France, Greece, Italy, Norway, The Netherlands, United Kingdom, Sweden, Switzerland and Yugoslavia

The European Organization for Nuclear Research formally came into being on 29 September 1954, when the twelve Member States signed the ratification of the convention establishing the organization. However, the name of the Council prevailed and, up to today, the organization is still referred to in literature simply as "CERN".

3.3 Location

CERN's facilities lie on the Franco-Swiss border close to the city of Geneva, in between the Jura Mountains and Lake Leman.

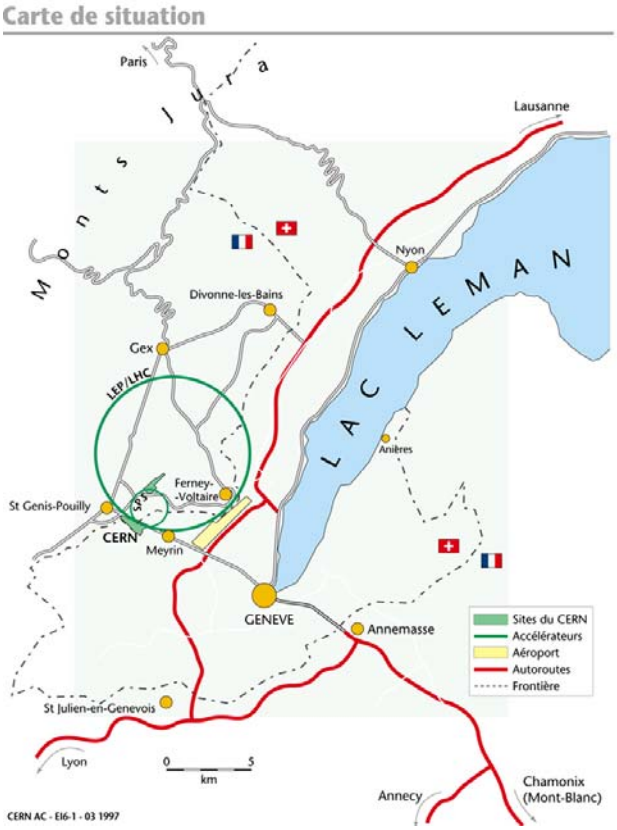


Figure II – CERN's Location

Figure III – Aerial View of CERN's surroundings showing also the experiment rings.

CERN is divided within two main sites:

- Meyrin was the first site of CERN to be built and it is the working place of the majority of its employees. It is also where the PS Complex (Positron Synchroton) is located. The border line between France and Switzerland crosses this site.

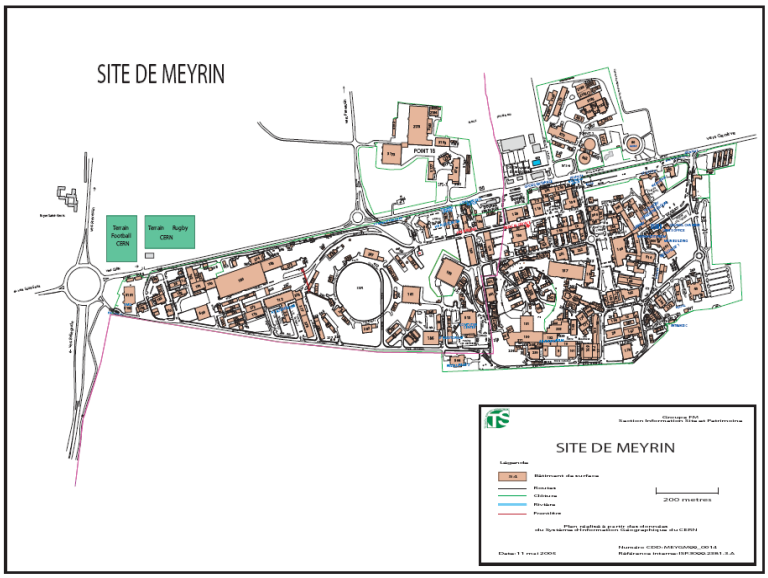


Figure IV – Site de Meyrin

- Prevessin is the second biggest site of CERN and it is located only in France.

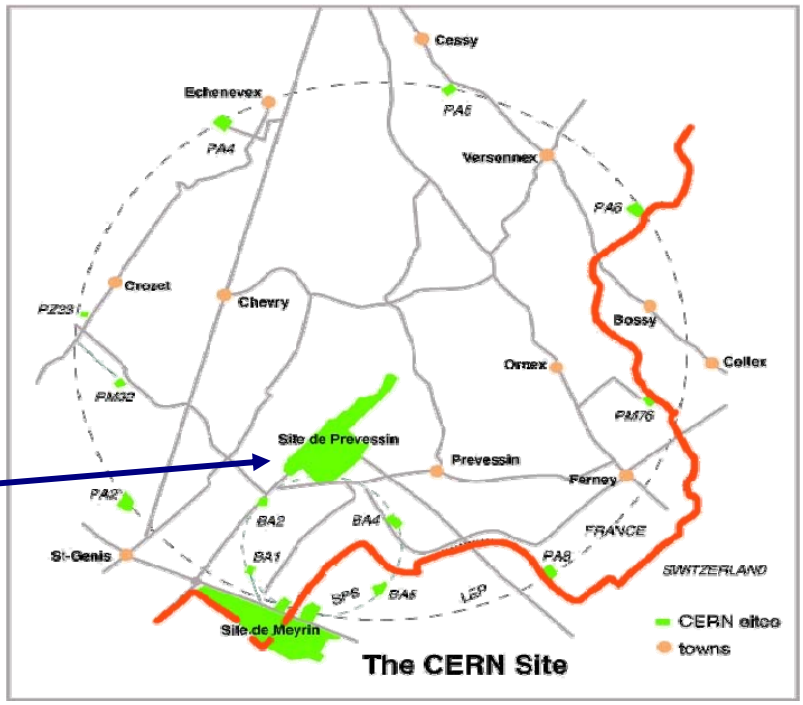


Figure V – Site of Prevessin

Other smaller sites of CERN are spread out along the experiments rings as shown in figure V in green. These sites serve as ground support to the experiments that CERN is conducting in the underground caverns.

3.4 Short description of the accelerators at CERN

A particle accelerator is a device that uses electric fields to propel electrically charged particles to high speeds and magnetic fields to contain them.
An ordinary household television set is, in fact, a very simple form of particle accelerator.

3.4.1 Short description of the PS

The Proton Synchrotron (PS) was the first major particle accelerator at CERN, built as a proton accelerator in 1959.

The PS machine is circular with a circumference of about 600 meters. It is a versatile machine which is used for accelerating antiprotons, protons, electrons, positrons and ions. *[A]*

The PS has been reused as the initial accelerator for the Super Proton Synchrotron (SPS) and it will be again reused in the same capacity for the Large Hadron Collider (LHC). *[4]*

3.4.2 Short description of the SPS

The Super Proton Synchrotron (SPS) is a particle accelerator built at CERN.
The SPS is installed in a circular tunnel of about 7 km of circumference and at an average depth of 50 meters below ground level.

The SPS has been used to accelerate antiprotons, electrons, positrons and heavy ions. The highlight of the SPS was its use as a proton-antiproton collider that lead to the discovery of the W and Z bosons for which Carlo Rubbia and Simon van der Meer obtained the Nobel Prize in the year of 1984.

Now, the SPS will be used as the final pre-injector for high-intensity proton beams for the LHC that is scheduled to begin operation in May of 2008, accelerating protons.
The SPS use as pre-injector will not interfere with the current fixed target research program and so the SPS will continue to be used to produce a neutrino stream for detection at the Italian Gran Sasso laboratory, 730 km from CERN. *[5]*

3.4.3 Short description of LHC

The Large Hadron Collider (LHC) is a particle accelerator and collider and is currently CERN's most important project. The LHC is presently under construction and it is expected to begin operation in May 2008 and to become the world's largest and highest energy particle accelerator.

The primary goal of the LHC is to study the structure of matter at the scale of TeV[1]. The Standard Model of particle physics is a theory that describes three of the four fundamental interactions in nature - electromagnetism, weak and strong forces – and that describes successfully the regime aforementioned. Most of the particles predicted by the Standard Model have been discovered in previous experiments, like the W and Z bosons at the SPS (CERN) and at the top quark at Tevatron (a similar experiment to the LHC, built at Fermi National Laboratory, in USA). The one missing particle that has not yet been detected is the Higgs Boson, thought to be the particle which gives mass to all others via its coupling to them. It is expected that this particle will be detected at the experiments at LHC. Apart from the goal specified previously, the LHC has a second goal: to discover new phenomena which have not been predicted by the Standard Model and could lead to new advances in theoretical physics. Those new phenomena could include supersymmetry, extra dimensions, quantum gravity, and a myriad of other different models that are collectively called Beyond the Standard Model of particle physics (BSM).

The LHC is funded and built in collaboration with over two thousand physicists from thirty-four countries, universities and laboratories.

The LHC is a colossal structure and a civil engineering challenge that requires careful planning. In 1995, the construction of the LHC was approved. The initial budget was 2.6 billion Swiss francs, with an additional 210 million francs towards the cost of the experiments. *[2]*

The collider is set up inside a circular tunnel with a circumference of almost 27 kilometres, at depths that range between 50 to 175 metres underground. The LEP (Large Electron-Positron Collider, CERN´s prior large scale accelerator) was previously installed in this concrete tunnel that has been enlarged and now has 3.8 metre of diameter.

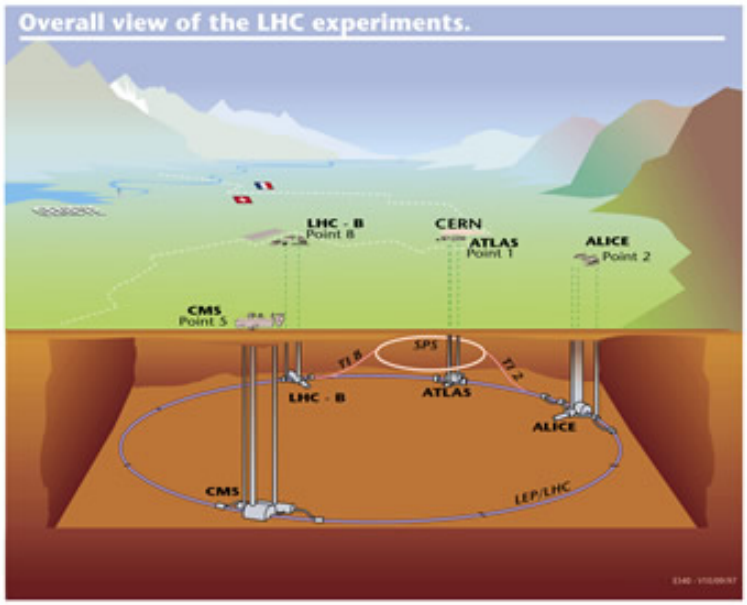


Figure VI – Overall View of the LHC experiments

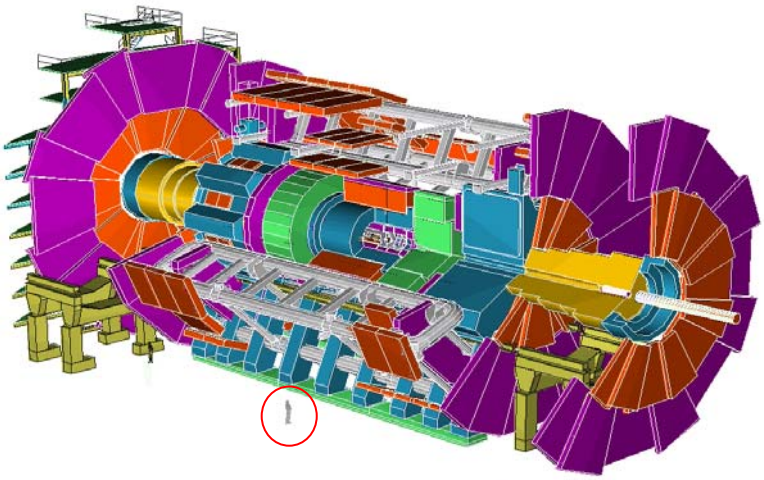
[1] In particle physics, time, length and energy are multiples of the same dimension. One teraelectron-volt (TeV) is the equivalent to $2x10^{-19}$m

Most of the tunnel's length is in France with only a small part in Switzerland. The collider is housed underground having the support of buildings in the surface that are holding auxiliary equipment such as compressors, ventilation equipment, control electronics and refrigeration plants.

The collider tunnel also contains two pipes enclosed within superconducting magnets that are cooled by liquid helium, each pipe containing a proton beam. The two beams travel in opposite directions around the ring. Additional magnets are used to direct the beams to four intersection points where interactions between them will take place.

Prior to being injected into the main accelerator, the particles are prepared through a series of systems that successively increase the particle energy levels. The first system is the linear accelerator that generates protons. Protons are then injected into the Proton Synchrotron (PS) and finally the Super Proton Synchrotron (SPS) can be used to further increase the energy of protons. The LHC can also be used to collide heavy ions.

This particles will be detected by six detectors that are being constructed at the LHC's tunnel intersection points.



ATLAS and CMS are the largest and they will serve as general purpose particle detectors. LHCb, ALICE, TOTEM, and LHCf are smaller and more specialized. *[2]*

Figure VII – Atlas Detector

All the work put into making the LHC run represents 5000 man years of engineering effort from CERN and its collaborating institutes.

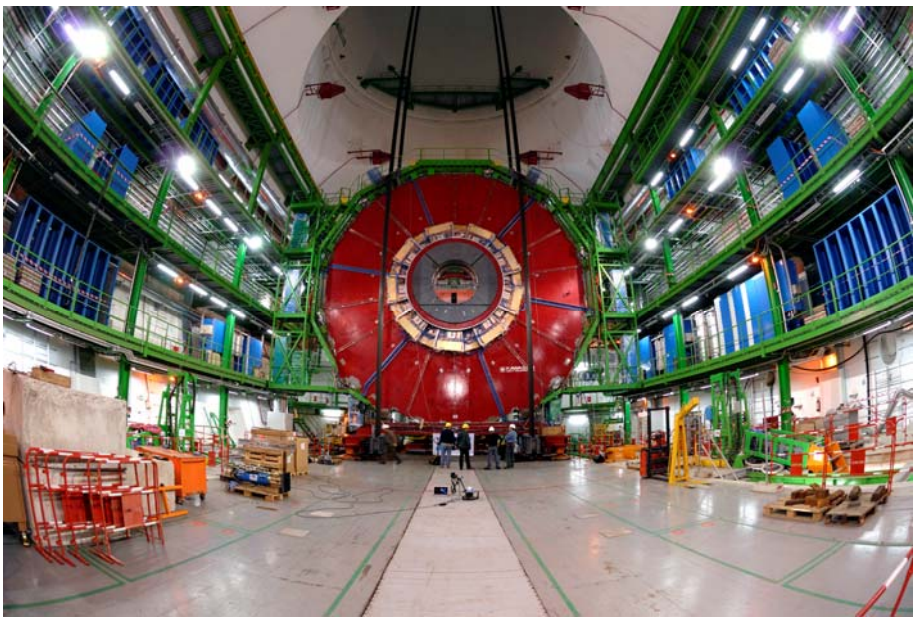


Figure VIII – CMS Detector Tunnel

3.5 The Environmental Section of the Safety Commission at CERN

For organizational purposes CERN is divided into several departments with distinct sizes and responsibilities.

This study was carried out within the Environmental Section of the Integrated Safety & Environment Group (SC\IE) that belongs to the Safety Commission of CERN, under the supervision of Sonja Kleiner, responsible for conventional environmental monitoring at CERN.

The environmental section of the Integrated Safety & Environmental Group monitors direct environmental impacts of the Organization's activities.

The section runs an extensive environmental monitoring programme covering both the radiological and conventional aspects that include:

- Surveillance of stray radiation in the environment;
- Monitoring of authorized radioactive releases;
- Analyses of radioactivity in environmental samples;
- Weekly checking of physical and chemical parameters of water in local streams receiving water from CERN;
- Periodic water sampling campaigns at specific points and times;
- Measuring concentrations of nitrogen oxides and ozone in the ambient air & accelerators emissions.

The Section assesses the results of the monitoring programmes and also, initiates corrective actions, if necessary. *[3]*

4. DESCRIPTION OF THE WATER SYSTEMS AT CERN

Most of the water used by CERN water systems is meant for cooling purposes.
Other water usages are for sanitary and industrial purposes.

4.1 Raw Water supply

At the present time, CERN's consumption of water is around 6 million of cubic meters per year.

The raw water supply for CERN comes from "Le Vengeron" pumping station that is located in Switzerland, as shown in figure IX. The water supplied to CERN is pulled from Lake Leman and it is treated as if it would be used for drinking purposes.

The supplier is SIG – SO (Service Industriels de Genève – Service des Eaux).

As the accelerators must never stop their normal functioning, it is fundamental that a secondary water supply is ensured at all times. This way, "La Berne" reservoir is maintained as a back-up solution in case of an eventual water supply problem of "Le Vegeron" *[A, Annex 7 – Supply - Water Origin]*

The following figure shows a schematic of the raw water supply to CERN:

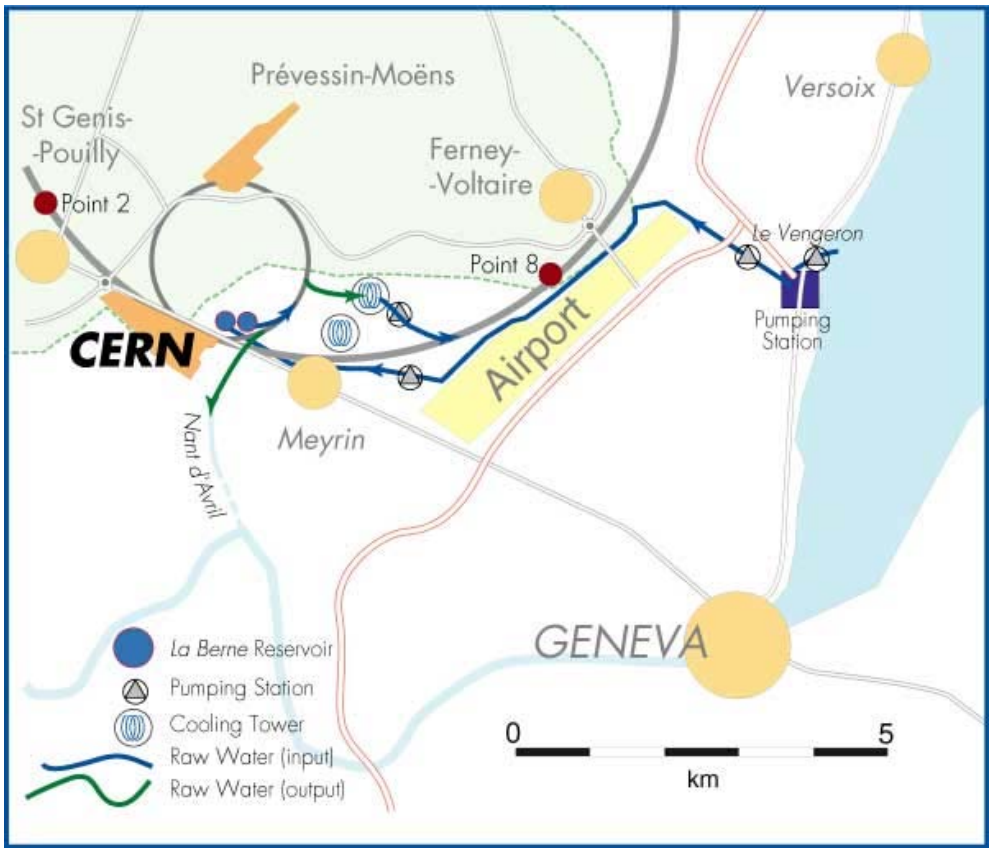


Figure IX - Map of CERN's raw water supply

4.2 Effluent Water

At CERN, there are two different water networks that release water in two distinct ways:

- The site drainage network;
- The sewerage drainage network.

Table 1 synthesizes the two networks through which CERN releases its effluent water:

Table 1 – CERN's water system: Types of water and its division according to disposal procedure

		Types of water	Receptor of Water
CERN Water System	CERN's drainage network	Cooling water	Rivers
		Meteoric water	
		Infiltration water	
	Sewerage drainage network	Sanitary water	Public sewage treatment plant
		Water from industrial processes	

The quality of the water from these networks is subjected to a monitoring programme that includes both the monitoring of water released from CERN installations and the evaluation of the impact of CERN effluents on the receiving water courses. This programme covers radiological and conventional issues.

4.2.1 The site drainage network

The site drainage network collects water that is considered to be clean and, as such, is released directly into local rivers and streams surrounding CERN sites without receiving any type of special treatment. This network deals with the biggest volume of water.

This network receives and disposes of water from the following sources:

- Cooling water;
- Meteoric water;
- Infiltration water.

4.2.1.1 Cooling water

Being the main topic of this study, cooling waters are described and analysed in a separated chapter numbered 4.3.

4.2.1.2 Meteoric water

Roads, parking places and roofs of CERN buildings are examples of impermeable surfaces that may accumulate water either during rainfall or snowfall. This water is then collected through the site drainage and released into local rivers and streams.

The two main sites at CERN discharge these waters into the rivers Nant d'Avril (Switzerland) and Le Lion (France). In more problematic situations, when the presence of oil is possible, the water is cleaned prior to the release at oil separators. (Annex 1 contains a description of the rivers that receives the biggest amount of water from CERN which is Nant d'Avril)

4.2.1.3 Infiltration water

Part of the meteoric water mentioned above, infiltrates the ground and reaches the underground tunnels of CERN. This water is collected and then pumped out of the tunnels into CERN's drainage network.

The LHC reaches depths of 175 meters and the SPS reaches depths of 50 meters. At these depths, it is possible that the infiltration water contains concentrations of natural hydrocarbons due to the nature of the geological conditions of the soil through which the water percolates. For these hydrocarbons not to appear in the water that CERN releases, the infiltration water is passed through oil-water separator units.

In addition, radioactivity that is produced during interactions of high-energy particles may leach out by means of the infiltration water that passes close to the concrete or earth near to the accelerator facilities. In order to appear in infiltration waters the radionuclides must be both soluble and long-lived (^{3}H and ^{22}Na). As a result, infiltration waters are always monitored before leaving any CERN site.

4.2.2 The sewerage drainage network

The sewerage drainage network receives water that is then directed to public sewage treatment plants that are located outside of CERN domain.

The water from this network can be organized into two groups:

- Sanitary water;
- Water from industrial processes.

4.2.2.1 Sanitary water

Sanitary water is normal waste-water that originates at CERN's main sites.
According to its source, this water is discharged to the public sewerage treatment plants either in Nant d'Avril (CH) and Allondon (FR) being, this way, treated outside of CERN before reaching any river.

4.2.2.2 Water from industrial processes

Apart from the sanitary water, CERN also discharges into the public sewerage network its industrial waters that result from activities such as:

- Surface treatment;
- Production of demineralised water.

The surface treatment workshops release water that may contain concentrated chemicals. As such, it is collected in specific pipes in order to be treated on-site before its release to the public sewerage network.

Continuous measurements of pH and detailed weekly analyses are carried out to control the efficiency of the on-site treatment.

The production of demineralised water may create industrial water which may be acid or alkaline. Thus, this water must be neutralized before its release into the local public sewerage treatment plant.

Detailed analyses are carried out to check the compliance of the effluents before release to the public sewage network.

4.3 Cooling water

4.3.1 General description of the functioning water cooling circuits

As previously stated, cooling water accounts for most of the water consumption at CERN. The water cooling circuits of CERN have the objective of refrigerating the accelerators and detectors, for example the electronic circuitry, the magnets or even the air surrounding these devices.

These systems use two types of water:

- The primary circuit contains raw water;
- The secondary circuit contains demineralised water.

The primary circuit (also called demineralised or closed circuit) is designed for reducing the temperature of the demineralised water in the secondary circuit.
In order to accomplish this, raw water is passed through heat exchangers where it absorbs the heat of the demineralised water of the secondary circuit. In cases, where the water needs to be further refrigerated, water chillers are used to actively transfer the heat through mechanisms of compression and decompression.

Then, the raw water loses the obtained heat in the atmospheric refrigerants where a flow of forced air reduces the raw water temperature, through a natural process of evaporation into the atmosphere. Thus, the raw water is again suitable to refrigerate the demineralised water of the secondary circuit, being again pumped underground and re-starting the cycle once more.

Figure X – Cooling Towers at CERN

The secondary circuit (also called semi-closed) of the cooling system is designed to refrigerate parts of the accelerator installations. For this purpose demineralised water is used, once water naturally contains many minerals and especially the water of the semi-closed cooling circuits because part of the water is evaporated and leaves behind its dissolved minerals.
The presence of these minerals makes the water a very good conductor of electricity, which in the vicinity of the high voltage accelerator would create the risk of dangerous sparks or short circuits. In this way, the secondary circuit of the cooling system has its

potentially conducting ions removed. The secondary circuits work in direct contact with the devices, thus cooling them. *[6]*

The following diagram illustrates well the functioning of a primary cooling circuit:

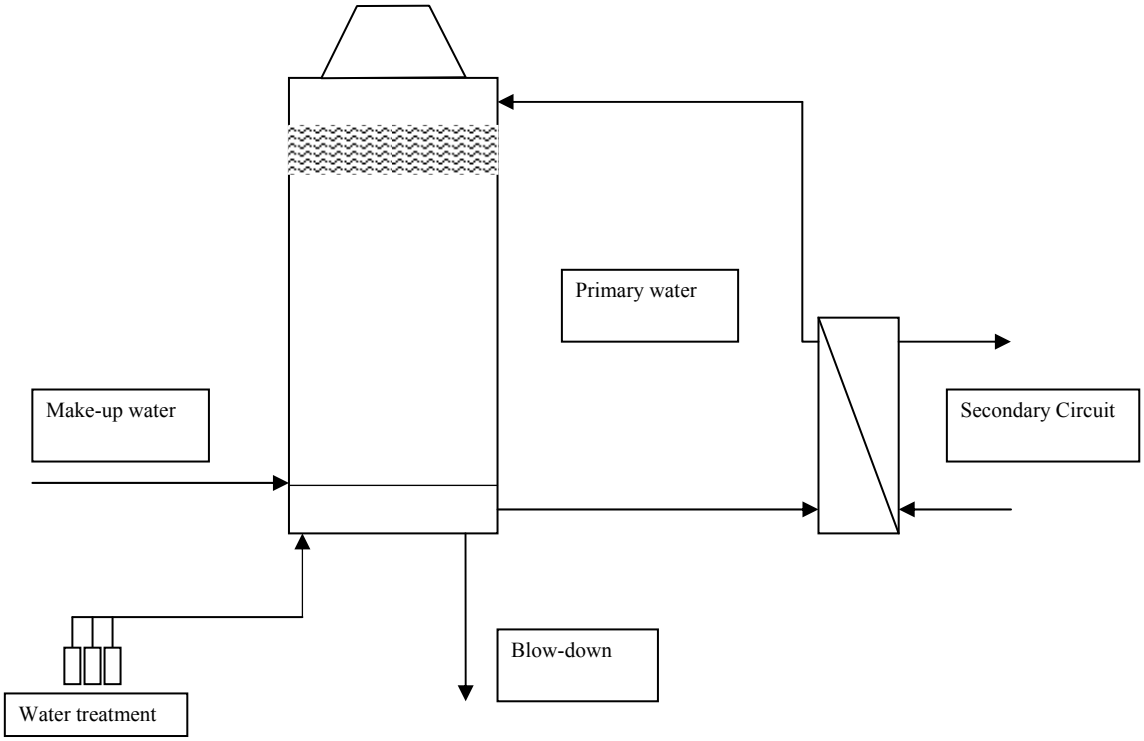


Figure XI – General diagram showing the functioning of a primary cooling circuit

De-concentration water is discharged so that make-up water can go into the cooling circuit in order to dilute the water inside the cooling circuit that due to evaporation has an increased value of conductivity.

Water treatment is used to maintain optimal condition as it will be detailed in the following chapters.

The Cooling and Ventilation Group of Technical Support Department (TS/CV) is in charge of the processes above described. They supervise all maintenance and repair work and have also the responsibilities of design and construction, which at the moment is dominated by works for the LHC. The Atlas and CMS areas have required completely equipped new cooling towers, pumps and underground cooling stations.

There were also many important modifications made to the cooling circuits. For example, previously the LEP's magnets were cooled by circuits of demineralised water. However, the superconducting magnets of the LHC now require being cooled by liquid helium to extremely low temperatures. This is responsibility of the Cryogenics Group. These water cooling circuits are still used to cool the equipment involved in producing the liquid helium, as well as the power converters, physics experiments and the magnets in the beam transfer tunnels. *[8]*

4.3.2 Types of water cooling circuits:

Within the general functioning system above described, three main types of water cooling circuits exist:

- Closed circuits;
- Semi-closed circuits;
- Open circuits.

The primary circuits of CERN above described are considered as semi-closed water circuits as the water inside is kept in a closed loop being only periodically discharged. These water discharges serve to ensure the cooling efficiency and to limit the mineralization of the water by the input of fresh raw water, also called make up water.

On the other hand, secondary circuits that were also detailed in the previous chapter are considered to be closed circuits. The conductivity at these circuits is kept low by means of ion exchangers.

Open circuits are cooling circuits were the water only passes through the system once. Most of CERN's previous water open cooling circuits were changed to semi-closed both for environmental and economical reasons related to a more efficient use of water.
The big majority of CERN cooling circuits are now semi closed or closed circuits. However, a few open circuits still exist in some old physics experiences representing in very small percentage of the total water cooling circuits at CERN.

5. CERN'S COOLING CIRCUITS

As seen before, the discharges from CERN's semi-closed and open cooling circuits are included in the site drainage network. Within those discharges, this study focuses on the ones done by CERN's semi-closed cooling circuits that represent the majority of the discharges.

CERN has a total of 24 cooling points for the semi-closed cooling systems that serve the LHC, SPS and PS. This implies a total of 69 cooling towers where different types of treatments take place.

The following map shows the LHC, SPS and PS points. It shows also the Prevessin and Meyrin sites and gives an overall view of the surrounding rivers to where CERN discharges water. All of CERN's water discharges done through the site drainage network (including CERN's cooling circuit discharges) are made into small local rivers being Nant d'Avril the main receiver (this river is further described in annex 1). All this water will ultimately flow to the Rhône (the big river on the right bottom corner).

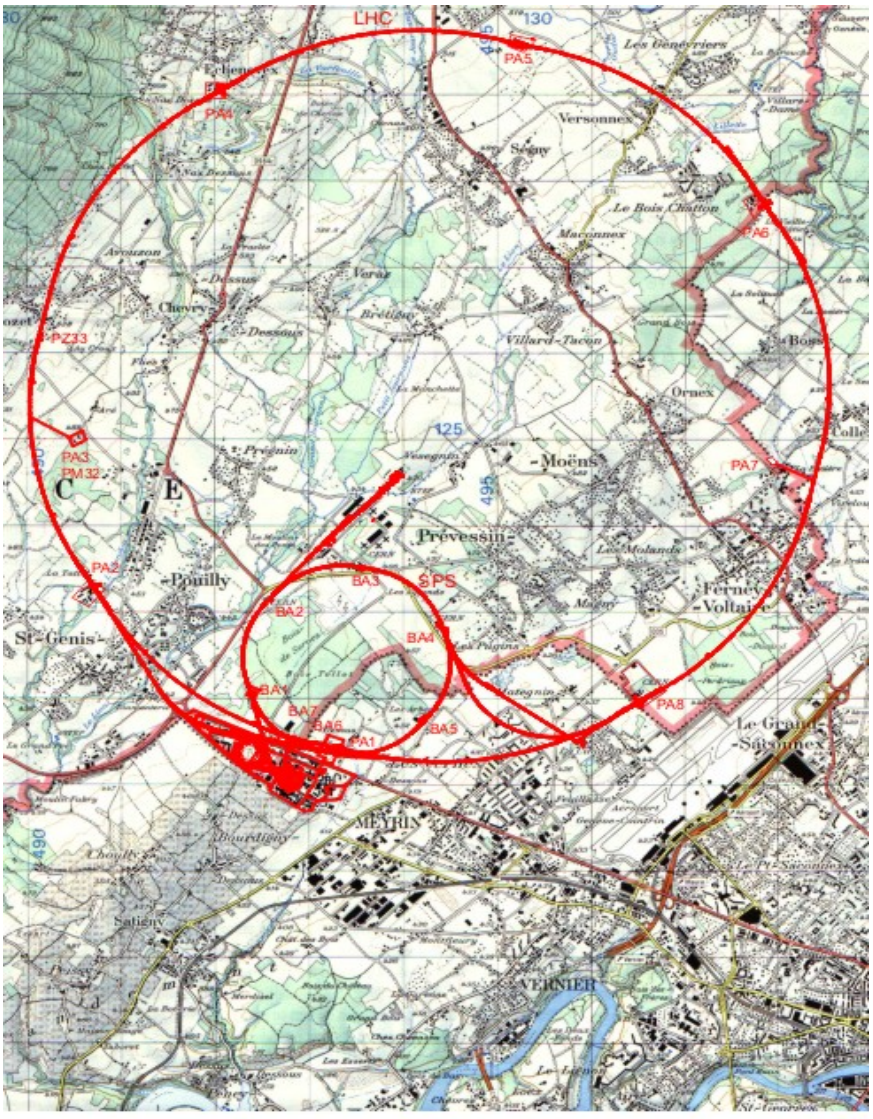


Figure XII – Map of CERN LHC, SPS and PS ground points

5.1 LHC cooling circuits

5.1.1 Water supply for the LHC

The distribution of raw water in the tunnel is done through LHC's point 1 where a pump makes the water circulate over the entire LHC tunnel, using two independent semi-loops 13km long. This pump supplies both underground installations (alcoves, fire hydrants in the tunnel) as well as surface installations through the access shafts around the LHC ring (air-conditioning, cooling towers, fire-fighting system).

This pump also supplies the water that is used as make-up water at the cooling towers throughout the LHC ring.
At the 7 LHC points numbered 1, 1.8, 2, 4, 5, 6 and 8 of figure XIII, cooling water is pumped in a surface station and supplied to various circuits.

The closed circuit has its make up water is supplied via point 1 of the LHC, by a central demineralised water production plant located in building 378.

5.1.2 Semi-closed cooling circuits of the LHC

The semi-closed water cooling circuits of the LHC is divided into 8 points with a total of 32 cooling towers. In total, they hold a volume of water of about 5100 m^3 that runs at very different flows ranging from 330 to 4500 m^3/h, removing a total heat of 294 MW from the water and releasing it into the atmosphere. *[A, Annex 2 – Description of CERN water systems]*

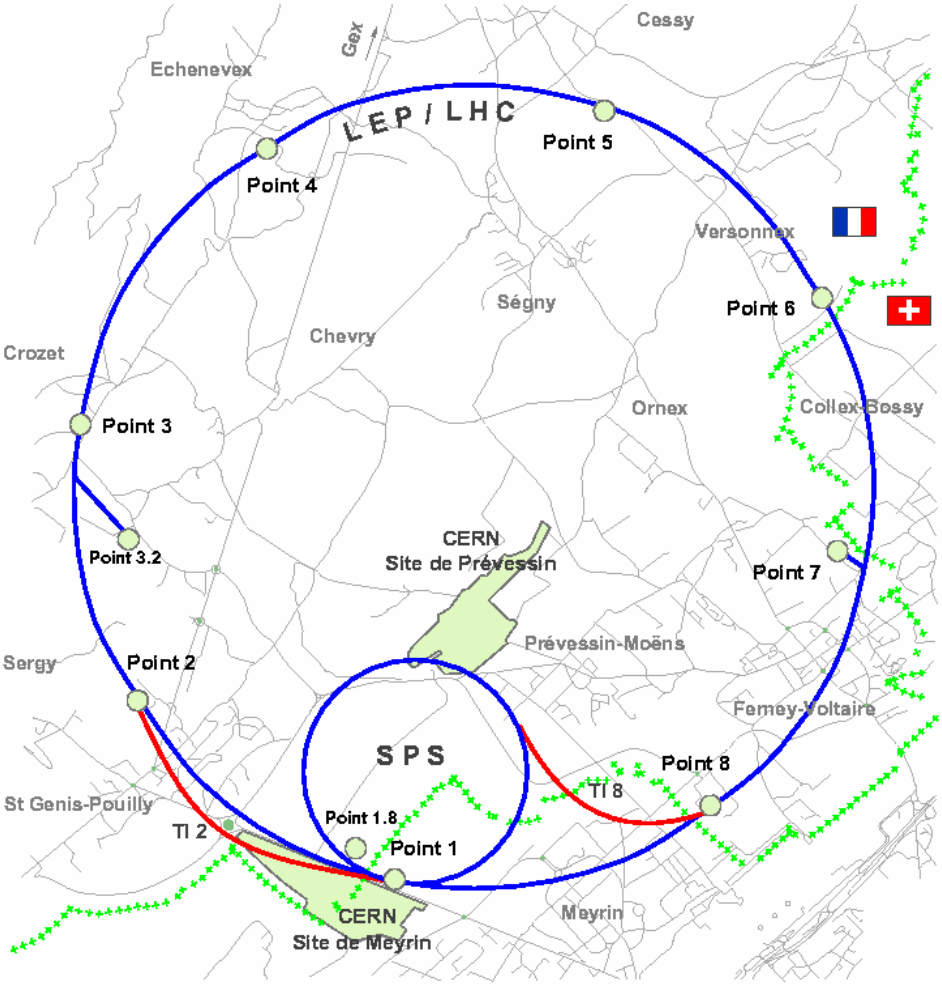
The next table is summarizing the LHC semi-closed cooling circuits.

Table 2 – LHC semi-closed cooling circuits

LHC Cooling Circuits	
Total Number of Cooling Towers	32
Total Volume of Water	5090 m^3
Flow Range	330 – 4500 m^3/h
Total Heat Extracted	294 MW

5.1.3 Closed cooling circuits of the LHC

The LHC closed water cooling circuits is distributed over 10 points.
The LHC closed circuits always hold much smaller volumes than the semi-closed water cooling circuits, although closed circuits exist in greater number and serve a greater variety of purposes.
These circuits generally contain demineralised water that will be supplied from a central demineralised water production plant located in building 378. Exceptionally, this water can be supplied through demineraliser cartridges.
These circuits do not discharge water into the environment although rare leakages of minor water volumes may occur.



Map of CERN sites and LHC access points

Figure XIII: LHC Layout

5.2 SPS cooling circuits

5.2.1 Water supply for the SPS

A supply line coming from Meyrin and going into the Prévessin site is responsible for the raw water supply. This water is used as make-up water for the cooling towers of building 863 (also called BA6) and the North Zone (Building 893).

The raw water supply of the SPS is basically the same as in the LHC area.

5.2.2 SPS semi-closed circuits

The semi-closed water cooling system of the SPS is divided into 3 points with a total of 11 cooling towers. In total, they hold a volume of water of about 5520 m3 that runs at very different flows ranging from 600 m^3/h to 3600 m^3/h, removing a total heat of 142 MW from the water and releasing it into the atmosphere. *[A, Annex 2 – Description of CERN water systems]*

On the next table, the SPS semi-closed cooling circuits are summarized.

Table 3 – SPS semi-closed water systems

SPS Water Systems	
Total Number of Cooling Towers	11
Total Volume of Water	5520 m^3
Flow Range	600 – 3600 m^3/h
Total Heat Extracted	142 MW

The SPS and LHC water cooling systems have a similar total volume of water but the LHC removes almost the double of heat. This happens because the SPS water cooling system was built much before the LHC water cooling system but also because the flows are in general bigger at the LHC water cooling systems.

SPS primary water usage

There are 3 cooling circuits in the SPS, West zone and North zone complex using primary water.

A pumping station (WS SPS) is circulating primary water from the 4 cells cooling tower (Building 863) in the SPS complex. There, it is supplying the heat exchangers in BA1, BA2, BA3, BB3, BA4 and BA5 with primary cooling water.
A 4 cells cooling tower of the North area (Building 893) is supplying the heat exchangers in BA80, BA81 (+ Turbo York for the chilled water production) and BA82 with primary cooling water.
A 6 cells cooling tower of the West area (Building 274) is supplying the heat exchangers (in the same building) with cooling water and a physics experiment in the building 180.

5.2.3 SPS closed circuits

Generally, secondary circuits in the SPS complex contain demineralised water that is produced in the demineralised water production plant at building 378. A distribution loop is running along the tunnel and rising at each shaft to supply the closed circuits on the SPS ring as well as the heating plant.

The demineralised water plants are equipped with an expansion tank that controls the pressure of the circuit. Conductivity is maintained by re-circulating the flow through demineralisation cartridges. *[A, Annex 2 – Description of CERN water systems]*

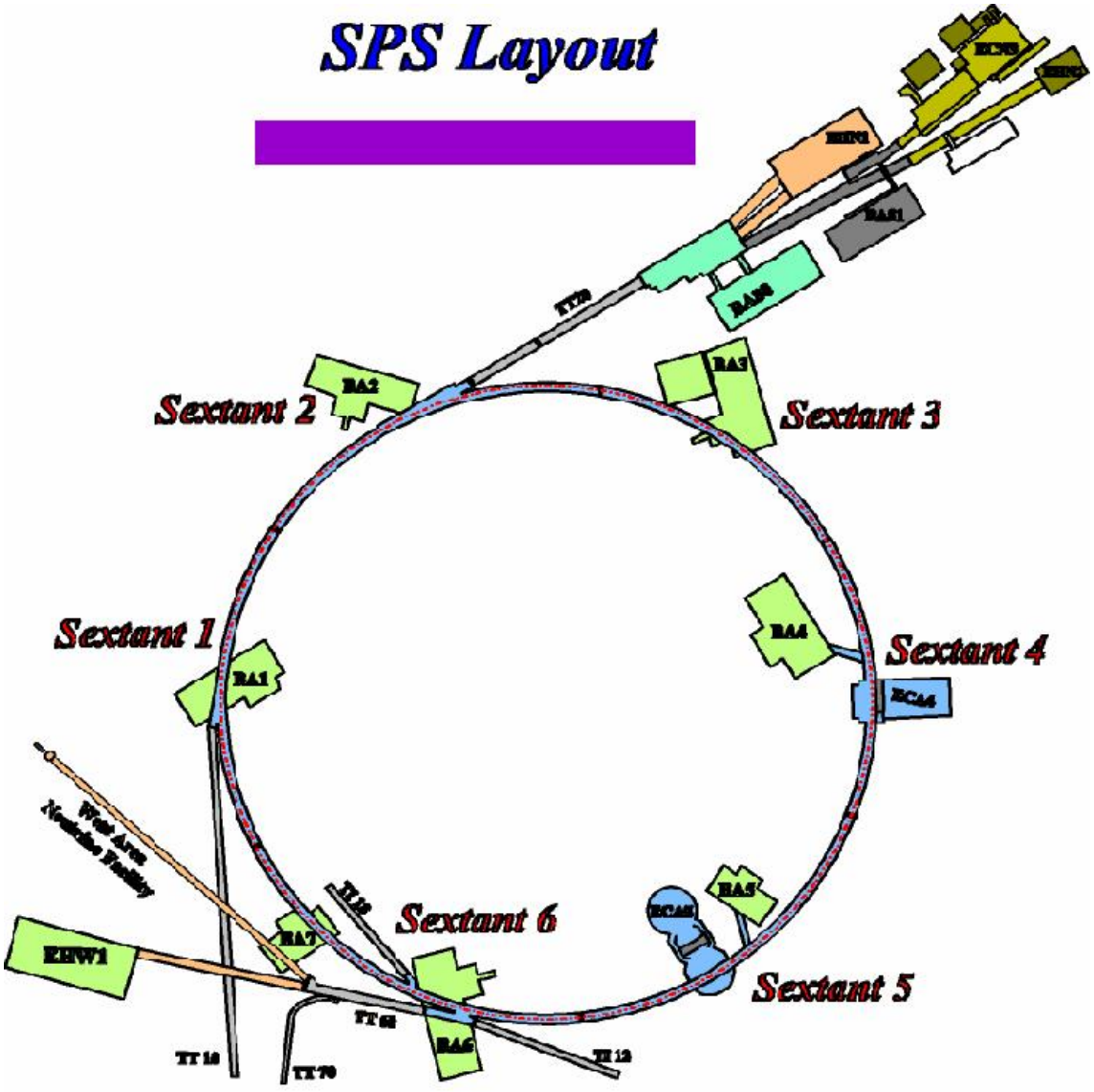


Figure XIV: SPS Layout

5.3 PS cooling circuits

PS is the first major particle accelerator at CERN. This way, the PS complex has cooling circuits that were constructed in 1960 along side with circuits that were constructed in 2001.

PS water systems are mostly used for the accelerator's cooling which includes: conventional magnets, SEPTA magnets, accelerating cavities, wave guides and auxiliary facilities.

However, part of the PS water systems is connected to other local experimental zones. This implies that some of the cooling stations may remain in use, even during the shut-down period, usually comprehended between November and March, when all the accelerators are inactive.

5.3.1 PS semi-closed circuits

The semi-closed water cooling system of the PS is divided into 13 points with a total of 26 cooling towers. In total, they hold a volume of water of about 400 m^3 that runs at very different flows ranging from 107 m^3/h to 900 m^3/h, removing a total heat of 54 MW from the water and releasing it into the atmosphere. *[A, Annex 2 – Description of CERN water systems]*

On the next table, the PS semi-closed cooling circuits are summarized.

Table 4 - PS semi-closed water systems

PS Water Systems	
Total Number of Cooling Towers	26
Total Volume of Water	412 m^3
Flow Range	107 – 900 m^3/h
Total Heat Extracted	54 MW

The cooling stations of the PS complex vary significantly on the cooling capacity, location and type of primary cooling circuit.

The raw water quality is the same as for the LHC and SPS areas.

5.3.2 PS closed circuits

The PS closed cooling circuit holds a great variety of circuits which mostly contain demineralised water.
This demineralised water is used to fill the accelerators cooling systems.
It is produced in two installations (Buildings 141 and 358) with a total capacity of 100 m^3 between two regeneration cycles. The quality of the demineralised water in each system is kept using interchangeable cartridges or rechargeable mixed-bed ion exchangers.

5.4 Accelerator water discharge systems

This work is focused on the discharges that reach the rivers. The discharges from the accelerator water system are included within the site drainage and are discharges that reach the rivers.

The annual amount of discharged cooling water from CERN circuits into the river "Nant d'Avril" in Switzerland is 0.43 x 10^6 m^3. It is the biggest volume of water discharged by CERN.

5.4.1 LHC Complex

The discharged water of the LHC complex arises mainly from 3 different sources:

- De-concentration of the cooling circuits;
- Natural drain water from the underground areas;
- Discharge water from other users such as small cooling circuits, residual water from sites as well as water arising from works such as civil engineering.

De-concentration is the main source of reject water from the LHC Complex.
This water is inserted in the cooling circuits to compensate the losses of water through evaporation and also to decrease the conductivity or other undesired parameters.

The evacuation procedure will depend on the nature of the water.
The 2 possible evacuation alternatives are described bellow:

- De-concentration of the semi-closed cooling circuits is collected by the two semi-loops in the underground, transferred into a recovery tank named PM 15 for analyses and, if compliant with the Suisse Laws, discharged into the river "Nant d'Avril" in Switzerland;
- Water from infiltration and meteoric sources is rejected directly into the nearest river located close to the LHC point;

5.4.2 SPS Complex

The SPS waste water contains the discharges from the cooling circuits as well as water that infiltrates into the tunnels. This waste water eventually contains also water from the leaks of the secondary circuit.

This water is divided into 3 different evacuation lines:

- The de-concentration water from the North Zone (building 893) is re-injected back into the cooling circuits of building 863;
- The de-concentration water from all the SPS ring (building 863) is evacuated into a Swiss river (Nant d'Avril). This is the major discharge from the SPS water system;
- The de-concentration water from the West Zone is evacuated into a French river (le Lion) from the Meyrin site.

5.4.3 PS Complex

There are various sources of waste water at the PS complex:

- Semi-closed cooling water discharges;
- Open circuits discharge;
- Infiltration water (including also eventual leaks from secondary circuits).

This water is discharged into the river "Nant d'Avril" in Switzerland.

6. ASSOCIATED RISKS OF COOLING CIRCUITS

Apart from the treatments necessary for technical reasons (like anti-scaling or anti-corrosion, in order to maintain the optimal running conditions of the cooling towers), a quite significant part of biocide treatments at CERN are dedicated to the prevention of the proliferation of *Legionella* bacteria once the infection caused by these bacteria are the biggest health risk from cooling towers.

Through their chimneys, cooling towers release, into the air, evaporated water that contains tiny particles of aerosols. These tiny particles are the vehicle for contracting the *Legionella* disease. If these particles contain *Legionella* bacteria, an outbreak could occur.

Therefore, the treatments for prevention of *Legionella* bacteria represent a significant part of the overall treatments and also of its environmental impacts due to those treatments.

6.1 Causes and Effects of the Legionnaire's disease

Legionnaires' disease is caused by a type of bacteria called *Legionella*.
Legionellosis is an infection caused by the bacterium *Legionella pneumophila*. *[13]*
According to US Center for Disease Control and Prevention, this disease has two distinct forms:

- Legionnaires' disease, the more severe form of infection which includes pneumonia;
- Pontiac fever, a milder illness.

Legionnaires' disease, according to the European Working Group for Legionella Infections, carries a mortality rate in the order of 10-15%, in otherwise healthy individuals. *[9]*

An infection by *Legionella* can be contracted through breathing in very fine droplets of water (named aerosols) that contain the bacteria. This infection can not be transmitted from person to person nor can it be contracted through the drinking of Legionella-contaminated water. *[11]*

The disease may present a series of symptoms ranging from flu-like illness to mental confusion or vomiting and diarrhoea. The incubation period normally ranges from 2 to 10 days with 3 to 6 days the typical illness onset time after exposure. *[B]*

Persons most at risk of falling ill to this bacterium are elderly people, as well as persons having chronicle lung diseases (like emphysema) or persons that are smokers.
Also persons that suffer from weak immune systems due to diseases like cancer, diabetes or kidney failure have a bigger possibility of succumbing to the *Legionella* bacteria.

6.2 Background on Legionnaire Disease

The first event that brought "the Legionnaire disease" forward to public knowledge took place in 1976, during a Philadelphia convention of the American Legion when a large number of war veterans suffered from an outbreak of this disease, having many succumbed to the disease effects. *[16]*

However, according to Dr. Makin (Directorate Manager for Medical Microbiology at The Royal Liverpool and Broadgreen University Hospitals in Liverpool, U.K), the legionnaires disease has been around much before that. Dr. Makin reported an attempt to trace the effects of the disease on man to a much earlier date. Taking samples from an ancient Roman bath they found *Legionella Pneumophila* bacteria, the precursor for the disease, in abundance within the pool. "*It is ironic*," states Dr. Makin, *"that the first victims of Legionnaires Disease could well have been the ancient Roman Legionnaires rather than the American Legionnaire". [14]*

6.3 Favourable Conditions for growth of Legionnaires disease bacteria

Low or even non-detectable, levels of this organism can colonize a water source and grow to high concentrations as long as the following conditions are gathered: *[16]*

- Stagnated water;
- Warm waters presenting temperatures within the range of 20° to 50°C, being the temperatures between 35 and 46 °C the ideal conditions;
- pH within the range of 5.0 and 8.5;
- Sediment with affinity for growth of commensal micro flora;
- Microorganisms such as algae, flavobacteria, and Pseudomonas, which supply essential nutrients for growth of Legionnaire disease bacteria;
- Protozoa that contain organism such as amoebae;

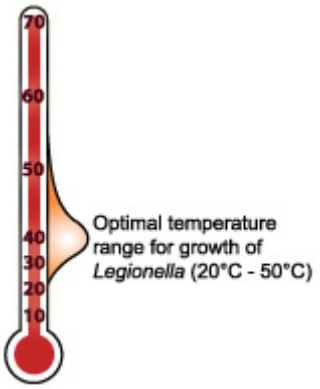


Figure XV: Optimal temperature range for growth of Legionella

6.4 Sources that may lead to an outbreak of Legionnaire disease bacteria:

Legionnaire disease bacteria are widely distributed over water systems around the world.

The most common sources of contaminated water are:

- Cooling towers, evaporative condensers and fluid coolers that use water evaporation to reject heat. These include many industrial processes that use water to remove excess heat;
- Domestic hot-water systems with water heaters that operate below 60°C and deliver water to taps below 50°C;
- Poorly maintained humidifiers and decorative fountains that create a water spray and use water at temperatures favourable to growth;
- Spas and whirlpools with aeration;
- Dental water lines, which are often kept at temperatures above 20°C and sometimes as warm as 37°C for patient comfort;
- Ice making machines.
- Possibly other systems such as stagnant water in fire sprinkler systems or warm water for eye washes or safety showers;

Any water system can be a potential source of bacteria as long as its water is within the conditions that support the growth of Legionnaire disease bacteria.

6.5 Cooling towers and alternatives

As stated in the previous chapter, CERN operates cooling towers that ensuring cooling for a variety of processes. The primary function of the cooling towers is to re-circulate water that would otherwise be run to waste.

Cooling towers can present problems at the level of Legionella outbreaks.
Not only do they run at favourable conditions for the growth of Legionella bacteria regarding parameters such as temperature, pH and high nutrient presence (due to the evaporation of water), but also these towers use water sprinklers with the purpose of maximizing the heat transfer process by creating tiny droplets of water called aerosols that, in turn, are the vehicle for transmission of the disease into humans. During the normal operation of a cooling tower the newly formed aerosols will escape into the environment through the tower exhaust. If Legionella is present in the water of the tower anyone breathing the air containing aerosols may suffer from an infection. Poorly maintained cooling towers have been accountable for outbreaks of Legionnaires' disease worldwide.

In order to remove the risk of Legionella outbreaks whilst keeping the cooling towers operating within the necessary conditions previously mentioned, biocide products are inserted into the water of the towers thus killing the Legionnaires' bacteria. However, the input of biocide is only efficient if accompanied by a careful plan of monitoring the water cooling plant for the presence of Legionella colonies.

Additionally, water cooled systems have a better efficiency over equivalent cooling systems also carrying similar risks. According to Bob Macleod-Smith (UK managing director of BAC Balticare), *"Typically water-cooled plants can be designed with a condensing temperature as much as 15 K lower than an equivalent air-cooled system"*. This represents a quite significant benefit once CERN's cooling circuits are required to operate at low temperatures. *[17]*

Figure XVI - Aspect of a CERN cooling tower during the winter

7. WATER TREATMENT IN CERN'S SEMI CLOSED COOLING CIRCUITS

7.1 Types of treatment

As mentioned in the previous chapter, CERN has many cooling circuits with an age range from 0 to almost 50 years and with quite different characteristics or even functions. This fact leads to a quite significant variance on the quantities and procedures of treatment at each specific cooling tower. Treatments are also varying in accordance to the results of the water analyses.

In order to apply these water treatments, CERN employs a sub-contracted company called NALCO France, "Water Treatment and Process Chemical Technologies".
NALCO Company supplies both the products that are inserted in the cooling circuits and the manpower for carrying out these treatments.

The treatments that NALCO performs for CERN can be grouped in two main categories and three semi-categories:

- Regular Treatment;
- Shock Treatment;
  - Preventive Shock Treatment;
  - Corrective Shock Treatment;

For the regular treatment at CERN's water cooling circuits, the quantities of product that are inserted vary only in accordance to the estimated volume of the cooling circuit.

As for the shock treatment, the product application is depending on the volume of the circuit in question but also on the results of the *Legionella* analyses accordance with the various threshold specified in the French regulation "Arrété du 13 Décembre 2004". It is also important to mention that shock treatment when applied is cumulative with the regular treatment.

All water treatments that are carried out by NALCO for CERN are supervised by CERN's TS-CV group. The effect of the water treatments is measured along with the global effect of CERN effluent discharges by the Environmental Section of SC-IE group.

7.1.1 Regular treatment

The regular treatment at CERN's water cooling circuits has the objective of controlling the level of growth of microorganism as well as preventing scaling or corrosion along the circuit.

Regular treatment is applied in a constant basis, whether its application is continuous or punctual, such as twice per week. The input procedure depends on the product but also on the cooling circuit that is being cooled.

Regular treatment at CERN uses the following products:

- Anti Corrosion and Anti Scaling Product (1246SH);
- Biocide (NALCO 4360);
- Biodetergent (NALCO 77393)

Anti-Corrosion and Anti-Scaling product

Anti-Corrosion product is inserted in the water in order to prevent the corrosion of the metal pipes that occurs due to the high concentration of salts in the water. The water in the cooling circuits reaches high concentrations of salt due to the evaporation of warm water at the cooling towers.
Anti-Scaling product is inserted in the water in order to prevent the appearance of scale that thwarts the optimal functioning of the treatment.

The Anti scaling and Anti corrosion product is present in the raw water of primary cooling circuits with a concentration of 20 to 40 ppm.

The effectiveness of anti-corrosion and anti-scaling product is affected by the conductivity of the water present in the cooling circuits.
RC is the ratio between the conductivity if the raw water that is coming in from Lake Leman and the conductivity of the water of the cooling circuits. This way, an RC of 2 implies that the conductivity of the water in the cooling towers is around 660 µS/cm, once that the normal conductivity for the raw water used at CERN is around 330 µS/cm.
In order to lower product consumption and to maximize the circuit efficiency, the water of the cooling circuits should maintain a ratio between 2 and 3.

Biocide

Biocide is any chemical substance that is capable of killing different forms of living organisms. The Biocide inserted in the water of CERN's cooling towers has the objective of stopping or reducing the growth of microorganisms in the cooling circuits to an acceptable level once these bacteria may represent a danger to health, as well as, temper with the good functioning of the cooling system.

The regular biocide product is used in the water of primary cooling circuits with a concentration of 1 to 4 ppm. This way, the quantity used at each cooling circuits varies according to the estimated volume of the circuit.

The biocide input procedures also varies from circuit to circuit due to the above mentioned specifications.

Input procedure can be:

- Automatic;
- Manual.

In the cooling circuits with automatic systems, the input is controlled by a machine that maintains a concentration of residual chlorine in the circuit up to 0,5 Cl_2 mg/l.

Else the input is done periodically and directly into the insertion basin of the cooling tower, from where it spreads to the rest of the circuit. This type of product insertion is named, punctual input.

Biodetergent

Biodetergent is placed in the water to enhance the effect of biocide. This product forces all the materials inside the pipes into suspension, thus making the microorganisms more vulnerable to the action of the biocide, increasing the effectiveness of the treatments and decreasing the amount of biocide that is necessary to use in order to reach a safe concentration level of microorganisms in the cooling circuits.

At a few cooling circuits at CERN, biodetergent is input automatically by a machine that controls its level on the water and keeps the product at a steady concentration, thus enabling using less biocide to obtain the same safety level. Other circuits only input biodetergent when applying more intense biocide treatment.

7.1.2 Shock Treatment

Shock treatments are applied in order to prevent that the concentration of *Legionella* bacteria increases above the threshold limit permitted by law.

In accordance to the French regulation "Arrété 13 of Décember of 2004" that concerns cooling towers and *Legionella*, CERN makes voluntary monthly check for this bacteria in each cooling circuit. This regulation mandates that treatment shall be applied whenever the number of UFC/l (units forming colonies per cubic meter) is above 1000.

Additionally, in a preventive spirit, CERN performs weekly checks in 3 specific circuits where outbreaks happened in the past. These circuits are Building 863, SF1 and STP18 that will be analysed in more detail in chapter 10. Furthermore, for the year of 2007, 5 monthly preventive shock treatments were performed at these 3 points regardless of the concentration shown in the water result analyses. It is important also to mention that these treatments were done over the summer which is the period when the *Legionella* outbreaks are more prone to occur.

The water analyses for the Legionella bacteria are performed in Laboratoire Marcel Mérieux – "Biologie Medicale Specialisée". The obtained results are classified into two categories, according to the degree of certainty of the result:

- Provisory – 1 week following the delivery of the sample;
- Definite – 2 weeks following the delivery of the sample.

The need for the use of this classification comes from the fact that the final result of the analyses takes 2 weeks and, in case of exceeding prescribed thresholds, the treatment should be applied as soon as possible. The use of these analyses is foreseen within the mentioned law. If after the provisory results treatment is done, treatment will not take place again when the definite results arrive unless an unlikely value of 10000 UFC/l surges.

In this way, according to the result proximity to 1000 UFC/l, treatment will be enforced or not directly after the provisory result arrives at CERN. When treatment is not applied after the provisional results, it may still be applied when the definite results are known. The application of shock treatments can be divided into 2 groups:

- Preventive Shock Treatment;
- Corrective Shock Treatment;

Preventive Shock Treatment

Preventive shock treatment takes place when the result of the analysis (either provisory or definite) is bellow 1000 UFC/l. Product is inserted in a concentration of 100 ppm.

Corrective Shock Treatment

Corrective shock treatment takes place when the result of the analysis (either provisory or definite) is above 1000 UFC/l. Product applied has a concentration of 100 ppm (results bellow 10000 UFC/l) or 200 ppm (above 10000 UFC/l). If the results are close to 100 000 UFC/l, the circuit will be fully stopped until results are again normal again.

All shock treatments in the water cooling circuits use the following two products that are always inserted into the cooling circuit at the same moment:

- Specific Legionella Biocide (NALCO 77352);
- Biodetergent (NALCO 77393).

Specific *Legionella* Biocide

Due to the reasons above mentioned, *Legionella* growth must be controlled.
This way, CERN makes a much tighter control over this parameter and applies in its cooling waters a specific product for controlling *Legionella* growth.

In most cases, the product insertion point is the injection basin at the cooling tower and from there the flow of the cooling circuit makes the product spread to the rest of the cooling circuit, thus reducing the concentration of the *Legionella* bacteria.

The specific *Legionella* biocide product is input, generally in a concentration of 100 ppm, except when a corrective shock treatment is taking place. In a corrective shock treatment, the quantity of this product may be doubled to 200 ppm, if the analyses present results above 10 000 UFC/l.
The quantity of specific *Legionella* biocide that is inserted into the circuits depends on the total volume of the circuit. For most cooling circuits at CERN, it is normal to insert the equivalent (in kilograms of product) to around 10 % of the total volume (in m^3). This way, if a circuit has 1500 m^3 of water the input will be 150 kg of specific *Legionella* biocide.

Biodetergent

This application of biodetergent in shock treatment has the objective of enhancing the effect of the specific *Legionella* biocide. This product forces all the materials inside the pipes into suspension, thus making the microorganisms more vulnerable to the action of the biocide, increasing the effectiveness of the treatments and decreasing the amount of biocide that is necessary to use in order to reach a safe concentration level of microorganisms in the cooling circuits.

Also, the ratio between the specific *Legionella* biocide and Biodetergent is fixed. This way, the quantity of inserted Biodetergent is generally equal to 10% of the total quantity of the specific *Legionella* treatment. When the circuits contain a machine for automatic input of biodetergent, the additional input is only of 5% in order to make the final 10%.

7.1.3 Overall view of the treatments

The information previously presented is summarized here in following tables. Table 5 shows the usage of products according to the type of treatment.

Table 5 – Product usage per type of treatment

Product	Regular Treatment	Shock Treatment
Anti Corrosion, Anti Scaling	Always	Never
Biocide	Always	Never
Specific *Legionella* Biocide	Never	Always
Biodetergent	Sometimes, depending on the cooling circuit	Always

Table 6 shows the quantity of products inserted per treatment type and the analyses results that lead to application of treatment in the cooling circuits.

Table 6 – Quantities of product applied per types of treatment and their application conditions

Type of Shock Treatment	Result of Analyses	Type of Analysis Result	Quantity of Specific *Legionella* Biocide	Quantity of Biodetergent
Preventive	< 1.000 UFC / l	Either provisory or definite	100 ppm	10% of specific Legionella Biocide
Corrective	> 1.000 UFC / l		100 ppm	
	> 10.000 UFC / l		200 ppm	
	> 100.000 UFC / l		200 ppm and circuit is stopped	

Table 7 shows the overall concentration of treatment products at CERN's cooling circuits.

Table 7 - Overall view of products concentration in cooling circuits

Product	Concentration of product in the water of primary circuit during treatment
Anti Corrosion, Anti Scaling	20 to 40 ppm
Biocide	1 to 4 ppm
Specific *Legionella* Biocide	100 ppm or 200 ppm, according to *Legionella* analyses results
Biodetergent	10% of normal biocide during regular treatment; 10% of *Legionella* biocide during shock treatment;

7.2 Specifications of products used

7.2.1 Anti-scaling and Anti-corrosion product

For anti-scaling and anti-corrosion purposes, CERN uses Kemazur 1246SH a product that is commercialized by NALCO. The following information has been extracted from the Material Safety Data Sheet (MSDS) provided by Nalco.

- The product main components are:
  - Water,
  - Polymers,
  - Phophono-carboxylic acids,
  - Zinc chloride,
  - Hydrochloric Acid
  - Tolytriazole.

- Some of the physical properties of the material are:
  Product has a pH < 1 and a freezing point of -15 ºC.

- The MSDS also specifies that product is toxic for aquatic life and that product can lead to harmful long term effects on environment.

Still in accordance with the MSDS, dangerous substances that product contains are listed below along with the Central Authentication Service (CAS) identification, the range of percentage of component and components possible hazards:

Table 8 – Components of anti-scaling and anti corrosion product

Nº CAS	Designation CEE	Percentage (%)	Safety Symbol of Chemical
7647-01-0	Hydrochloric Acid	10 - 20	C
29385-43-1	Tolyltriazole	1 - 5	Xn
7646-85-7	Zinc Chloride	1-10	C, N

Description: C (Corrosive), Xn (Harmful), N (Dangerous for the environment);

The Anti scaling and Anti corrosion product is present in the raw water of primary cooling circuits with a concentration of 20 to 40 ppm. Nalco is responsible for controlling and adjusting this value.

Further information about Tolytriazole and Zinc Chloride, as well as, the complete MSDS is presented in annexes 9 and 10.

7.2.2 Biocide Product

Regular biocide treatment uses a Nalco product with the following code "4360 TAB".
The following information has been extracted from the Material Safety Data Sheet (MSDS) provided by the manufacturer Nalco.

- This product is an oxidizing Biocide.
- Product has a pH of 3.6.
- The MSDS specifies that product utilization is dangerous for aquatic life and that it may lead to the formation of AOX (Adsorbable Organic Halides).

Still in accordance with the MSDS, dangerous substances that product contains are listed below along with the CAS identification, the range of percentage of component and components possible hazards:

Table 9 – Components description for the routine biocide product

Nº CAS	Designation CEE	Percentage (%)	Safety Symbol of Chemical
16079-88-2	Bromine-5,5-Dimethylimidazolidine – 2,4 – dione	50 – 70	O, C, N
118-52-5	1,3-Dichlorine-5,5-Dimethylhydantoin	20 – 30	O, C, N
89415-87-2	1,3-Dichlorine-5 Ethyl – 5 methylhydantoin	10 – 20	O, N, T

Description: C (Corrosive), Xn (Harmful), N (Dangerous for the environment), T (Toxic), O (Oxidizing);

Further information on these compounds, as well, as the complete MSDS is presented in annexes 9 and 10.

7.2.3 Specific Legionella Biocide

The Specific *Legionella* Biocide has a NALCO number 77352.
This product is a non-oxidizing biocide and it is commercialized by NALCO.
The complete MSDS of this product is presented in Annexes 9 and 10.

It is specified in the material data safety sheet (MSDS) that this product is dangerous for aquatic life and that it may lead to the formation of AOX or to high values of Chemical Oxygen Demand.

This product is a preparation in aqueous solution containing dangerous substances that are described in the following table:

Table 10 – Components description for the specific *Legionella* biocide product

Nº CAS	Designation CEE	Percentage (%)	Safety Symbol of Chemical
26172-55-4	5 – Chlorine – 2 – Methyl – 4 – isothiazoline 3 – one	1.5 – 1.8	T, N
2682-20-4	2 – Methyl – 4 – isothiazoline 3 – one	1.5 – 1.8	T, N

Description: N (Dangerous for the environment), T (Toxic);

7.2.4 Biodetergent

The Biodetergent used for water treatment at CERN's cooling circuits has NALCO number 77393. This product is commercialized by NALCO.

Its main components are:
Water, D-Glucopyranose, Oligomeric, Decyl Octyl Glycosides.

Dangerous substances that this product contains are shown in table below:

Table 11 – Components description for the biodetergent product

Nº CAS	Designation CEE	Percentage (%)	Safety Symbol of Chemical
68515-73-1	D – Glucopyranose, Oligomeric, Decyl octyl glycosides	5 -15	Xi
110615-47-9	D – Glucopyranose, Oligomeric, C10 – C16 – Alkyl Glycosides	1 – 10	Xi

Description: Xi (irritant);

Further information on these compounds, as well, as the complete MSDS is presented in annex 9.

8. APPLICABLE REGULATION ON EFFLUENT WATER

The regulation parameters and values on water vary substantially from country to country but for effluent water, in general, they can commonly be divided into two main groups:

- Effluent water discharge limits;
- Water quality objectives for streams and rivers.

The first set of limits concerns values to be measured in the water before the discharge into the environment whereas the seconds set of limits refers to values that are to be measured in the receiving rivers a few meters downstream of the outlet, after discharge and after the effluent water has mixed with the river water.

8.1 European Union regulation

The Council Directive 76/464/EEC of 4 May 1976 on pollution caused by certain dangerous substances discharged into the aquatic environment of the Community was one of the first water related Directives to be adopted.
The directive had the ambitious objectives of regulating potential aquatic pollution by thousands of chemicals already produced in Europe at that time. The Directive covered discharges to inland surface waters, territorial waters, inland coastal waters and ground water.

In 1980 the protection of groundwater was taken out of 76/464/EEC regulated under the separate Council Directive 80/68/EEC on the protection of groundwater against pollution caused by certain dangerous substances.

The Council Directive 76/464/EEC will now be integrated in the Water Framework Directive. Article 22 together with Article 16 of the Water Framework Directive (2000/60/EC) set out the transitional provisions for the existing Directive on discharges of certain dangerous substances (76/464/EEC).

In 2006, the Directive 76/464/EEC has been codified as 2006/11/EC.

The Directive 76/464/EEC introduced the concept of list I and list II substances, which were listed in the Annex. The purpose of the Directive is to eliminate pollution from list I substances and to reduce pollution from list II substances.

List I:

List I included a number of groups and families of pollutants from which certain individual substances were to be selected on the basis of:

- Persistence;
- Toxicity;
- Bioaccumulation.

In 1982, the Commission communicated a list to the Council (OJ C 176 of 14 July 1982, p. 3) that included 132 "candidate list I substances".
This list contained certain individual substances which belong to the following families and group of substances, with the exception of those which are biologically harmless or which are rapidly converted into substances which are biologically harmless:

- Organohalogen compounds and substances which may form such compounds in the aquatic environment;
- Organophosphorus compounds;
- Organotin compounds;
- Substances in respect of which it has been proved that they possess carcinogenic in or via the aquatic environment;
- Mercury and its compounds;
- Cadmium and its compounds;
- Persistent mineral oils and hydrocarbons of petroleum origin, and persistent synthetic substances which may float, remain in suspension or sink and which interfere with any use of the water.

Up to now, 18 individual substances of the "candidate list I" have been regulated in five specific Directives (also called "daughter directives") setting emission limit values and quality objectives on a Community level.
These Directives were the first mandatory minimum requirements for an approach based on best technical means (later known as best available techniques or BAT).

The regulation of other "candidate list I substances" was suspended in the beginning of the 1990s due to the preparation of a more comprehensive and integrated permitting system for industrial installations. In 1996, the Directive on integrated pollution prevention and control, the IPPC directive (96/61/EC) was adopted. The Directive includes the emission limit values for the 18 list I substances of the specific directives as minimum requirements for large installations.

List II:

List II includes groups and families of substances that have a deleterious effect on the aquatic environment. It also consists of all the individual list I substances that have not been regulated on Community level yet. As there are only 18 'real' list I substances, all the other 114 substances of the "candidate list I" and the groups and families of substances listed under list I must be considered as list II substances.

List II contains the families and groups of substances as follows:

- The following metalloids and metals and their compounds:

Zinc	Copper	Nickel	Chromium
Lead	Selenium	Arsenic	Antimony
Molybdenum	Titanium	Tin	Barium
Beryllium	Boron	Uranium	Vanadium
Cobalt	Thallium	Tellurium	Silver

- Biocides and their derivatives not appearing on list I;
- Substances which have a deleterious effect on the taste and/or smell of the products for human consumption derived from the aquatic environment. As well as, compounds liable to give rise to such substances in water;
- Toxic or persistent organic compounds of silicon, and substances which may give rise to such compounds in water, excluding those which are biologically harmless or which are rapidly converted in water into harmless substances;
- Inorganic compounds of phosphorus and elemental phosphorus;
- Non persistent mineral oils and hydrocarbons of petroleum origin;
- Cyanides, fluorides;
- Substances which have an adverse effect on the oxygen balance, particularly: ammonia, nitrites.

For the relevant pollutants of list II, Member States must establish pollution reduction programmes including water quality objectives according to Article 7 of the Directive 76/464/EEC.

Progress in properly implementing list II substances that are regulated under Article 7 of the Directive proved to be very slow. In the beginning of the 1990s, the Commission decided to start infringement procedures against most of the Member States. Most of the cases are before the European court of Justice and there have been already several rulings against Member States.

8.2 French regulation

Regarding France, the following regulation was consulted:

- Arrêté du 2 février 1998 relatif aux prélèvements et à la consommation d'eau ainsi qu'aux émissions de toute nature des installations classées pour la protection de l'environnement soumises à autorisation;

- Arrêté du 13 décembre 2004 relatif aux installations de refroidissement par dispersion d´eau dans un flux d´air soumises à autorisation au titre de la rubrique nº2921;

- Décret n°91-1283 du 19 décembre 1991 relatif aux objectifs de qualité assignés aux cours d'eau, sections de cours d'eau, canaux, lacs ou étangs et aux eaux de la mer dans les limites territoriales;

- Arrêté modifié du 20 novembre 1979 relatif à la lutte contre la pollution des eaux (application du décret n°78-218 du 23 février 1973);

- Guideline value taken from the French national water quality evaluation system *SEQ-EAU, March 2003 (green quality class);*

- Guideline value (quality objective) from the French Décret n°91-1283 du 19 décembre 1991.

The following table was done based of the previously mentioned documents:

Table 12 – French limits for effluents and quality objectives for river water

Parameter	French limits (A. 02.02.98)	French limits (A. 13.12.04)	Quality Objective Limits for river water after CERN outlets [2] ("Eaux salmonicoles")
Temperature	30	30	< 21.5°C and the difference between the temperatures of river water before and after the outlet should be less than 1.5°C [3]
pH	5.5-8.5	5.5-9.5	Maintain a pH between 6 and 9 after the outlet
Conductivity	-	-	120 -3000 µS/cm [4]
Dissolved O_2	-	-	50% of values measured during one month ≥ 9 mg/l; 100% of values measured during one month ≥ 7 mg/l; [5]
Turbidity	-	-	35 NTU (Nephelometric turbidity unit) [5]
Suspended matter	-	-	25 mg/l [6]
BOD_5(Biochemical oxygen demand after 5 days)	30	30	3 mg/l O_2 [6]
COD (Chemical oxygen demand)	125	125	30 mg/l O_2 [5]
DOC (Dissolved organic carbon)	-	-	7 mg/l C^4
Ammonium	-	-	1 mg/l NH_4
Nitrites	-	-	0.01 mg/l NO_2 [6]
Nitrates	-	-	10 mg/l NO_3 [5]
Chlorides	-	-	100 mg/l Cl^- [5]
AOX (Adsorbable organic halogens)	1 mg/AOX	1 mg/AOX	-
Copper	0.5 mg/l Cu	-	0.04 mg/l Cu dissolved [6]
Zinc	2 mg/l Zn	-	0.3 mg/l Zn
Iron	5 mg/l Al + Fe	-	-
Aluminium	5 mg/l Al + Fe	-	0.2 mg/l Al dissolved [5]
Lead	0.5 mg/l Pb	-	10 µg/l Pb [5]
Hexavalent Chromium (Cr^{VI})	0.1 mg/l Cr^{-VI}	Lower than detection limit	-
Cadmium	0.2 mg/l Cd	-	0.09 µg/l Cd [5]
Nickel	0.5 mg/l Ni	-	12 µg/l Ni [5]
Cyanides	0.1 mg/l CN^-	Lower than detection limit	0.2 µg/l CN^- [5]
Total hydrocarbons	10 mg/l	-	-

[2] Décret n°91-1283 du 19 décembre 1991 relatif aux objectifs de qualité assignés aux cours d'eau, sections de cours d'eau, canaux, lacs ou étangs et aux eaux de la mer dans les limites territoriales.
[3] Arrêté modifié du 20 novembre 1979 relatif à la lutte contre la pollution des eaux (application du décret n°78-218 du 23 février 1973).
[4] Guideline value taken from the French national water quality evaluation system *SEQ-EAU, March 2003 (green quality class).*
[5] Guideline value (quality objective) from the French Décret n°91-1283 du 19 décembre 1991.

8.3 Swiss regulation

The main regulation for effluent control and protection of the environment is the "*Ordonnance sur la protection des eaux, OEaux 814.201, du 28 Octobre 1998*".

This regulation is built upon two main principles:

1. Protect surface waters and subsoil waters against the harmful action and to allow their durable use.
2. To this end, all the measurements performed under the terms of the present regulation must take into account the ecological objectives laid down for water.

The following table compiles the values extracted from the "*Ordonnance sur la protection des eaux, OEaux 814.201, du 28 Octobre 1998*".

Table 13 – Limits for effluents and quality objectives for river water from OEaux[6]

Parameter	Limits for CERN's effluents	Quality Objectives Limits for river water after CERN outlets
Temperature	30°C	< 25°C and the difference between the temperatures of river water before and after the outlet should be less than 3°C
pH	6.5-9	No alteration in river water before and after the outlet
Conductivity	-	Not defined
Dissolved O_2	-	No reduction of O_2
Turbidity	-	No turbidity (except during rainfalls)
Suspended matter	20 mg/l	No forming of mud
BOD_5 (Biochemical oxygen demand after 5 days)	20 mg/l O_2 (7)	2-4 mg/l O_2
COD (Chemical oxygen demand)	-	-
DOC (Dissolved organic carbon)	10 mgl/ C	1-4 mg/l C
Ammonium	2 mg/l N	0.2 mg/l N
Nitrites	0.3 mg/l N	-
Nitrates	-	5.6 mg/l N
Chlorides	-	100 mg/l Cl^- (7)
Chlorine	0.05 mg / l of Cl_2	-
AOX (Adsorbable organic halogens)	0.1 mg/l X	-
Copper	0.5 mg/l Cu	0.005 mg/l Cu
Zinc	2 mg/l Zn	0.02 mg/l Zn
Iron	2 mg/l Fe (7)	1 mg/l Fe dissolved (7)
Aluminium	10 mg/l Al (7)	0.1 mg/l Al dissolved (7)
Lead	0.5 mg/l Pb	0.01 mg/l Pb
Hexavalent Chromium (Cr^{VI})	0.1 mg/l Cr-VI	0.002 mg/l Cr-VI
Cadmium	0.1 mg/l Cd	0.2 µg/l Cd
Nickel	2 mg/l Ni	0.01 mg/l Ni
Cyanides	0.1 mg/l CN^-	-
Total hydrocarbons	10 mg/l	0.05 mg/l (7)

[6] Ordonnance sur la protection des eaux, "*OEaux 814.201, Octobre 1998*".
[7] Guideline value from the Swiss "*Ordonnance sur le déversement des eaux usées*" (no longer in force).

Another Swiss regulation also consulted was the "*Ordonnance sur le registre des rejets de polluants et des transferts de déchets et de polluants dans les eaux usées (ORRTP)*" of 15 of december of 2006.

The purpose of this regulation is to assure, by means of registers, the access of the public to information concerning the rejections of pollutants, the transfers of waste and the transfers of pollutants into used water.

This regulation states limit values for emission of pollutants. However, these values are not stated in concentration in the receiving mean or in the effluent but they are stated in total quantity per year.

The following table presents some values for total annual discharges in rivers extracted from the "*Ordonnance sur le registre des rejets de polluants et des transferts de déchets et de polluants dans les eaux usées*".

Table 14 – Values for annual discharges in Swiss rivers

Parameter	Limits for annual discharges in Swiss rivers (kg/ year)
Arsenic and compounds (expressed as As)	5
Cadmium and compounds (expressed as Cd)	5
Copper and compounds (expressed as Cu)	50
Chrome and compounds (expressed as Cr)	50
Nickel and compounds (expressed as Ni)	20
Lead and compounds (expressed as Pb)	20
Zinc and compounds (expressed as Zn)	100
Adsorbable Organic Halogens (AOX)	1000
Chlorides (express as total Cl)	2 000 000
Total Organic Carbon (express as C total or DCO3)	50 000
Aromatic Polycyclic Hydrocarbons	5
Cyanides	50
Fluorides (expressed as total F)	2000
Total Nitrogen	50000
Total Phosphorus	5000

8.4 Other regulation cases

For comparison purposes, this work has looked into the environmental regulations of other countries. This was accomplished in order to get a better grasp of which values and parameters most effectively control an organization with the size and characteristics of CERN.

8.4.1. Portuguese regulation

The Portuguese base law of water is now the "Decreto-Lei n. 236/98" of 1 of August of 1998 that came to replace the previous "Decreto-Lei n. 74/90" of 7 of March of 1990.

The main objective of this document is to establish rules, norms, criteria and quality objectives with the purpose of protecting the aquatic environment, as well as, improving the quality of the water taking into account its main uses.

The present document stipulates the requirements that must be met when using the water for the following purposes:

- Water for Human Consumption;
- Water for support of aquatic life explored by man;
- Water for bathing areas;
- Water for irrigation.

Therefore, setting requirements for discharges of residual waters into the environment (water or soil), with the goal of supporting the quality of the aquatic mean and the protection of public health and soils.

Chapter VI of this document concerns the protection of water against pollution cause by the discharges of residual waters. With the objective of reducing or eliminating the pollution caused by this source, 2 European directives are transposed:

- Directive nº 76/464/CEE of the council in 4 of May, regarding pollution caused by the release of specific dangerous substances into the aquatic environment;
- Directive nº 80/68/CEE of the council in 17 of December, regarding the underground water protection caused by the release of specific dangerous substances.

Chapter VI of this document could be applied to CERN's discharge of residual waters. The document sets 2 types of values that any company discharging water into rivers must respect:

- The emission limit values;
- The water quality objectives in the receiving watercourses.

The emission limit values:

The emission limit values specify a maximum value that an effluent must not present. This limit is a monthly average, defined as the arithmetical averages of the daily averages referent to all working days of the month. The monthly limit can not be

exceeded. The daily value is obtained from a representative sample of the residual water that can never exceed the double of the monthly value.

The following table shows the discharge emission limits that must be respected for each type of pollutant.

Table 15 – Emission limits for discharge of effluents in Portugal

Emission Limits for Discharge of Effluents according to Portuguese Law nº 236/98		
Parameter	**Limit**	**Units**
Temperature	Increase of 3º [8]	Celsius
pH	6.0-9.0 [9]	Sorensen scale
Conductivity	-	-
Dissolved Oxygen	-	-
Turbidity	-	-
Smell	Must not be detectable in dilution of 1 to 20	-
Colour	Must not be visible in dilution of 1 to 20	-
Suspended matter	-	
Total Suspended Solids	60	mg/l
BOD_5 (Biochemical oxygen demand after 5 days)	40	mg/l O_2
COD (Chemical oxygen demand)	150	mg/l O_2
DOC (Dissolved organic carbon)	-	-
Sulphide	1	mg/l S
Sulphite	1	mg/l SO_3
Sulphate	2000	mg/l SO_4
Total Phosphorus	10	mg/l P
Nitrogen Ammoniac (NH_4)	10	mg/l NH_4
Total Nitrogen	15	mg/l N
Aldehyde	1	mg/l
Ammonium	-	-
Nitrites	-	-
Nitrates	50	mg/l NO_3
Chlorides	-	-
Free Chlorine	0.5	mg/l Cl_2
Total Chlorine	1.0	mg/l Cl_2
Phenol	0.5	mg/l C_6H_5OH
Oils and Greases	15	mg/l
Mineral Oils	15	mg/l
Detergents (Sulphate of Lauril and Sodium)	2	mg/l
AOX (Adsorbable organic halogens)	-	-
Total hydrocarbons	-	-
Total Copper	1	mg/l Cu
Total Zinc	-	-
Total Iron	2	mg/l Fe
Total Aluminium	10	mg/l Al
Total Lead	1	mg/l Pb
Total Manganese	2	mg/l Mn
Total Arsenic	1	mg/l As
Total Chromium	2	mg/l Cr
Hexavalent Chromium (Cr^{VI})	0.1	mg/l Cr^{-VI}
Total Cadmium	0.2	mg/l Cd
Total Nickel	2.0	mg/l Ni
Total Mercury	0.05	mg/l Hg
Total Cyanides	0.5	mg/l CN
Total metals	-	-

[8] Regarding the temperature of the receiving river measured 30 meters downstream after the discharge of the residual water.
[9] Daily average must be between 5,0 and 10,0

The water quality objectives in the receiving watercourses:

The water quality objectives refer to the limit values that should not be exceeded in the receiving rivers downstream after the effluent water is discharged.

Table 16 – Water Quality Objectives for Rivers in Portugal

Water Quality Objectives according to Portuguese Law nº 236/98		
Parameter	**Limit**	**Units**
Temperature	30	Celsius
Temperature Variation	3	Celsius
pH	5.0 to 9.0	Sorensen Scale
Dissolved Oxygen	50	% of saturation
BOD_5 (Biochemical oxygen demand after 5 days)	5	mg/l O_2
Nitrogen Ammoniac (NH_4)	1	mg/l N
Total Phosphorus	1	mg/l P
Chloride	250	mg/l Cl
Sulphates	250	mg/l SO_4
Chlorfenol	100	µg/l
Aromatic Hydrocarbon	100	µg/l
Anionic Tensides Substances	0.5	mg/l
Pesticides – Total amount	2.5	µg/l
Pesticides – Per compound	0.5	µg/l
PCB (Polychlorinatedbiphenyls)	20	µg/l
Nitrogen of Kjeldhal	2	mg/l N
Total Cyanide	0.05	mg/l CN
Total Arsenic	0.1	mg/l As
Total Cadmium	0.01	mg/l
Total Lead	0.05	mg/l
Total Chromium	0.05	mg/l
Total Copper	0.1	mg/l
Total Mercury	0.001	mg/l
Total Nickel	0.05	mg/l
Total Zinc	0.5	mg/l

Conditions required for conformity:

- The limits set by this document are cumulative with the discharges values set by the regional government.

- Whenever two limits for the same parameter exists the values to be considered is always the most demanding of the two criteria. This is valid both for the emission limit values and for the water quality objectives.

- When it is not possible to avoid dilution, the control of the parameter must be done taking into account the dilution factor, that shall be calculated upon the flow of the discharge and the dilution and they must be measured simultaneously at the time of the sampling.

- The residual waters will be considered as in conformity if the obtained values obey the following conditions in all parameters:
  - The average of the monthly values for each substance does not surpass the corresponding limit;
  - The daily average does not go above the double of the limit value, during the whole month and for each substance.

8.4.2 German regulation

Concerning the German regulation, "Bekanntmachung der Neufassung der Abwasserverordnung vom 17. Juni 2004" was consulted.

This regulation is particularly interesting because its values are not only specific for cooling water but also for cooling water before it is mixed with other effluents, which is the situation that this work is analysing.

The following table was made considering some of the values present in this legislation:

Table 17 - Emission Limits for Discharge of Effluents according to German regulation

Emission Limits for Discharge of Effluents according to German regulation		
Parameter	**Limit**	**Units**
COD (Chemical oxygen demand)	40	mg/l O_2
Total Phosphorus	3	mg/l P
Chlorine Dioxide (Expressed as Cl_2)	0,2	mg/l Cl_2
AOX (Adsorbable organic halogens)	0,15	mg / l X

It is important to notice that the value for AOX is specific for cooling waters that are exposed to biocide treatment which is exactly the situation occurring at CERN.
This German value for AOX is similar to the value present in the Swiss regulation, which specifies 0,1 mg / L AOX for effluent water.

The German Legislation considers as well eco-toxicological tests for the situation of cooling waters exposed to biocide treatment. These tests will be further described ahead in this work. The GL value represents the dilution level at which a wastewater sample causes less than 20% inhibition on the measured species. The previously mentioned document considers a GL value of 12 for cooling water before mixing with any other type of water and a GL value of 32 effluents from chemical industry.

8.4.3 Spanish regulation

The Spanish regulation "ORDEN MAM/85/2008, de 16 de enero" included in the Spanish "Ley de Aguas", establishes the technical criteria for the assessment of the damages to the public water domain and the norms for sampling and analysing residual water. The following table present the emission limits set by the above regulation:

Table 18 - Emission Limits for Discharge of Effluents according to Spanish Regulation

Emission Limits for Discharge of Effluents according to Spanish Regulation		
Parameter	**Limit**	**Units**
Temperature	Increase of 3º	Celsius
pH	5.5 - 9	Sorensen scale
Electrical Conductivity at 20ºC	1000	µS/cm
Colour	200	mg Pt /L
Total Suspended Solids	25	mg/l
BOD_5 (Biochemical oxygen demand after 5 days)	7	mg/l O_2
COD (Chemical oxygen demand)	30	mg/l O_2
Sulphate	250	mg/l SO_4
Total Phosphorus	0.4	mg/l P
Total Nitrogen	3	mg/l N
Total Ammonium	1	mg/l
Nitrates	50	mg/l NO_3
Chlorides	200	mg/l
Total Chlorine	0,005	mg/l Cl_2
Phosphates	0.7	mg/l
Biocides and other products	0.001	mg/l
Total Copper	0.005	mg/l Cu
Total Zinc	0,03	mg/l Zn
Total Iron	2	mg/l Fe
Total Lead	0.05	mg/l Pb
Total Manganese	1	mg/l Mn
Total Arsenic	0.05	mg/l As
Total Chromium	0.05	mg/l Cr
Total Cadmium	0.005	mg/l Cd
Total Nickel	0.05	mg/l Ni
Total Mercury	0.001	mg/l Hg
Total Cyanides	0.04	mg/l CN

Note: This legislation is presented here only as information because it was not integrated in the rest of the study once it was found on the end of the work.

The values above presented are lower than most of the consulted regulations for important parameters such as Total Chlorine, BOD_5 (Biochemical oxygen demand after 5 days), COD (Chemical oxygen demand) and metals in general (Zinc in particular). It is also the only consulted regulation to present an emission limit for conductivity.

8.4.4 Canadian regulation

Canada began in 1984 to develop regulation on water in order to create the Canadian Water Quality Guidelines. This regulation is subdivided into four categories:

- Canadian Water Quality Guidelines for the Protection of Aquatic Life;
- Canadian Water Quality Guidelines for the Protection of Agricultural Water Uses;
- Guidelines for Canadian Drinking Water Quality;
- Guidelines for Canadian Recreational Water.

Within the Water Quality Guidelines, this work was focused on the Guidelines for the Protection of Aquatic Life. These guidelines have been developed to reduce the effects that human activities have on aquatic plants and animals and on the environment itself. Chemical inputs and changes in the physical qualities of the water can put a strain on some aquatic organisms, making them more susceptible to disease or injury.

The information found in the these guidelines is hereby synthesized in the following table:

Table 19 - Canadian Water Quality Guidelines for the Protection of Aquatic Life

Canadian Water Quality Guidelines for the Protection of Aquatic Life		
Parameter	**Limit**	**Units**
Cadmium	0.017	µg/l
Copper	2-4	µg/l
Cyanide (as free CN)	5	µg/l
Hexavalent Chromium Cr^{VI}	1.0	µg/l
Iron	300	µg/l
Lead	1-7	µg/l
Nickel	25-150	µg/l
Nitrate	13 000	µg/l
Nitrite	60	µg/l
Oxygen, dissolved	5500-9500	µg/l
pH	6.5-9	Sorensen Scale
Temperature	(10)	Celsius
Zinc	30	µg/l

[10] Temperature:
Thermal Stratification: Thermal additions to receiving waters should be such that thermal stratification and subsequent turnover dates are not altered from those existing prior to the addition of heat from artificial origins.
Maximum Weekly Average Temperature: Thermal additions to receiving waters should be such that the maximum weekly average temperature is not exceeded.
Short-term Exposure to Extreme Temperature: Thermal additions to receiving waters should be such that the short-term exposures to maximum temperatures are not exceeded. Exposures should not be so lengthy or frequent as to adversely affect the important species.

8.5 Synthesis of all values and discussion on the possibility of creating a CERN internal regulation

CERN due to its statue as a non profitable international research organization is not obliged to follow the national regulations of its host countries (France and Switzerland).

However, CERN is a front line research organization and makes self control that most times is much sticker than what the French or Swiss laws mandate. It is also a European Organization that is support by European countries and so the laws of those countries can also be taken into account, as well as the regulation of the European Community. (e.g. European Directives)

This way, for comparison purposes, the following tables were done.

The first two tables show the emission limit values for the discharge of effluents in Switzerland, France, Portugal, and Germany.

The last table presents the water quality objectives for concentration of pollutants in receiving water courses in Switzerland, France, Portugal and Canada.

The strictest values within these countries were marked in bold for easier consultation.

Table 20 - Emission Limits for Discharge of Effluents for several countries (part I)

Emission Limits for Discharge of Effluents						
Parameter	**Units**	**Swiss limits (OEaux)**	**French limits (A. 02.02.98)**	**French limits (A. 13.12.04)**	**Portuguese Limit (236/98)**	**German Limits**
Temperature	Celsius	30	30	30	Increase of 3º	-
pH	Sorensen scale	6.5-9	5.5-8.5	5.5-9.5	6.0-9.0	-
Smell	-	-	-	-	Must not be detectable in dilution of 1 to 20	-
Colour	-	-	-	-	Must not be visible in dilution of 1 to 20	-
Suspended matter	mg/l	**20**	35	35	60	-
BOD_5 (Biochemical oxygen demand after 5 days)	mg/l O_2	**20**	30	30	40	-
COD (Chemical oxygen demand)	mg/l O_2	-	125	125	150	**40**
DOC (Dissolved organic carbon)	mg/l C	**10**	-	-	-	-

Table 21 - Emission Limits for Discharge of Effluents for several countries (part II)

Emission Limits for Discharge of Effluents						
Parameter	**Units**	**Swiss limits (OEaux)**	**French limits (A. 02.02.98)**	**French limits (A. 13.12.04)**	**Portuguese Limit (236/98)**	**German Limits**
Sulphide	mg/l S	-	-	-	**1**	-
Sulphite	mg/l SO_3	-	-	-	**1**	-
Sulphate	mg/l SO_4	-	-	-	**2000**	-
Total Phosphorus	mg/l P	-	-	-	10	**3**
Nitrogen Ammoniac (NH_4)	mg/l NH_4	-	-	-	**10**	-
Total Nitrogen	mg/l N	-	-	-	**15**	-
Aldehyde	mg/l	-	-	-	**1**	-
Ammonium	mg/l N	**2**	-	-	-	-
Nitrites	mg/l N	**0.3**	-	-	-	-
Nitrates	mg/l NO_3	-	-	-	**50**	-
Chlorides	mg/l Cl^-	-	-	-	-	-
Free Chlorine	mg/l Cl_2	-	-	-	**0.5**	-
Total Chlorine	mg/l Cl_2	-	-	-	**1.0**	-
Chlorine Dioxide (Expressed as Cl_2)	mg/l Cl_2	-	-	-	-	**0,2**
Fenol	mg/l C_6H_5OH	-	-	-	**0.5**	-
Oils and Greases	mg/l	-	-	-	**15**	-
Mineral Oils	mg/l	-	-	-	**15**	-
Detergents (Sulphate of Lauril and Sodium)	mg/l	-	-	-	**2**	-
AOX (Adsorbable organic halogens)	mg/l AOX	**0.1**	1	1	-	**0,15**
Total hydrocarbons	mg/l	**10**	**10**	-	-	-
Total Copper	mg/l Cu	**0.5**	**0.5**	-	1	-
Total Zinc	mg/l Zn	**2**	**2**	-	-	-
Total Iron	mg/l Fe	**2**	5 [11]	-	2	-
Total Aluminium	mg/l Al	10	**5** [12]	-	10	-
Total Lead	mg/l Pb	**0.5**	**0.5**	-	1	-
Total Manganese	mg/l Mn	-	-	-	2	-
Total Arsenic	mg/l As	-	-	-	1	-
Total Cromium	mg/l Cr	-	-	-	2	-
Hexavalent Chromium (Cr^{VI})	mg/l Cr^-_{VI}	**0.1**	**0.1**	Lower than detection limit	**0.1**	-
Total Cadmium	mg/l Cd	**0.1**	0.2	-	0.2	-
Total Nickel	mg/l Ni	2	**0.5**	-	2.0	-
Total Mercury	mg/l Hg	-	-	-	0.05	-
Total Cyanides	mg/l CN^-	**0.1**	**0.1**	Lower than detection limit	0.5	-
Total metals	mg/l	-	-	**15**	-	-

[11] The French regulation considers a limit for Aluminium and Iron together. This way, the concentration of both of these pollutants in reject water must not exceed 5 mg/l of Fe + Al.

Table 22 - Quality Objectives for Water in Receiving Water Courses for several countries

Quality Objectives for Water in Receiving Water Courses					
Parameter	**Units**	**Swiss limits (OEaux)**	**French Limits (Eaux Salmonicoles)**	**Portuguese Limit (236/98)**	**Canadian Limits**
Temperature	Celsius	< 25	**< 21.5**	30	-
Temperature Variation	Celsius	3	**1.5**	3	Must not exceed maximum weekly average
pH	Sorensen Scale	No alteration in the river water before and after the outlet	Maintain a pH between 6 and 9 after the outlet	5.0 to 9.0	6.5-9
Conductivity	µS/cm	-	120 -3000	-	-
Dissolved O_2	mg/l	No reduction of O_2	50% of values measured during one month ≥ 9 mg/l; 100% of values measured during one month ≥ 7 mg/l;	50% of saturation	5.5 - 9.5
Turbidity	-	No turbidity (except during rainfalls)	35 NTU (Nephelometric turbidity unit)	-	-
Suspended matter	-	No forming of mud	**25**	-	-
BOD_5(Biochemical oxygen demand after 5 days)	mg/l O_2	2-4	**3**	5	-
COD (Chemical oxygen demand)	mg/l O_2	-	30	-	-
DOC (Dissolved organic carbon)	mg/l C	**1 to 4**	7	-	-
Total Phosphorus	mg/l P	-	-	**1**	-
Ammonium	mg/l N	**0.2**	1 [12]	1	-
Nitrites	mg/l NO_2	-	**0.01**	-	0.06
Nitrogen of Kjeldhal	mg/l N	-	-	2	-
Nitrates	mg/l N	**5.6**	10 [13]	-	13
Chlorides	mg/l Cl^-	**100**	**100**	250	-
Chlorfenol	µg/l	-	-	**100**	-
AOX (Adsorbable organic halogens)	mg/l	-	-	-	-
Sulphates	mg/l SO_4	-	-	**250**	-
Total hydrocarbons	mg/l	**0.05**	-	-	-
Aromatic Hydrocarbon	µg/l	-	-	**100**	-
Anionic Tensides Substances	mg/l	-	-	**0.5**	-
Pesticides – Total amount	µg/l	-	-	**2.5**	-
Pesticides – Per compound	µg/l	-	-	**0.5**	-
PCB (bifenilospoliclorados)	µg/l	-	-	**20**	-
Arsenic	mg/l As	-	-	**0.1**	
Copper	mg/l Cu dissolved	0.005	0.04	0.1	**0.002 to 0.004**
Zinc	mg/l Zn	**0.02**	0.3	0.5	0.03
Iron	mg/l Fe dissolved	1	-	-	**0.3**
Aluminium	mg/l Al dissolved	**0.1**	0.2	-	-
Lead	mg/l Pb	**0.01**	**0.01**	0.05	0.001 to 0.007
Hexavalent Chromium (Cr^{VI})	mg/l $Cr-^{VI}$	0.002	-	-	**0.001**
Cadmium	µg/l Cd	0.2	0.09	10	**0.017**
Nickel	µg/l Ni	**10**	12	50	25 to 150
Total Chromium	mg/l	-	-	**0.05**	-
Total Mercury	mg/l	-	-	**0.001**	-
Cyanides	µg/l CN^-	-	**0.2**	-	5

[12] Value expressed in mg/l NH_4
[13] Value expressed in mg/l NO_3

CERN discharges its effluents to rivers both in Switzerland and France.

These discharges are subjected to the legislation above mentioned. For some of the parameters of the legislations of these two countries, the discharge limits for effluents vary substantially.

A good example is the parameter AOX. While Switzerland mandates a concentration in effluent water not superior to 0.1 mg/l of AOX, the correspondent value in France is only of 1 mg/l. This represents a factor 10 difference.

The procedure adopted by CERN up to now has been to always select the lowest limit of both regulations but this procedure may imply that CERN is using overly strict limits.

On the other hand, CERN is subsided by 26 member states and is inserted in the European Union, so both the communitarian and the regulation of these countries should be considered as well.

Conversely, establishing a full coherent internal set of regulations requires an extensive work of research that was already outside the scope of this study.

For these reasons above mentioned and, taking advantage both of this study and previous experience in this field by CERN's staff, CERN has instead issued an internal memorandum holding a recommendation from SC/IE Environmental group to TS/CV department that is containing a selection of parameters and values taken from the regulation of member states regulation concerning the emission limits for CERN's effluent water.

This memorandum was including the values present in the following table:

Table 23 – Recommended Emission Limits for the Discharge of CERN's cooling water

Emission Limits for Discharge of Effluents		
Parameter	**Units**	**Value**
Temperature	Celsius	**30**
pH	Sorensen Scale	**6.5 - 9**
Conductivity	µS/cm	**100 – 900**
Suspended matter	mg/l	**20**
DOC (Dissolved organic carbon)	mg/l C	**10**
COD (Chemical oxygen demand)	mg/l O_2	**40**
AOX (Adsorbable organic Halides)	mg/l X	**0.1**
Zinc	mg/l Zn	**2**
Free Chloride	mg/ l Cl_2	**0.5**
Free Brome	mg/ l Br_2	**0.5**

The limits hereby presented shall figure in a future CERN internal regulation. These limits correspond to the source term, meaning the water that is discharged from the cooling circuits prior to mixing with any other effluents.

The internal memorandum also mentions the limits at the fence (after mixing with other types of waters). These limits will be the same with the exception of the chlorine and bromine values that are both of 0.05 mg/l.

9 SAMPLING CAMPAIGN

Having in mind the goal of assessing the impact of the water discharged by CERN in the environment, a sampling campaign was initiated in order to gain a better knowledge of the quality of the water discharged and of the impact of certain points in the overall discharge.

9.1 Selection of measuring points

It was decided to make analyses in 3 points of CERN's water systems. These points were the cooling circuits at SF1 and building 863 and the RAMSES station point PA1 that measures the final release.

The selection of the measuring points was done considering the following aspects:

For Points SF1 of LHC and Building 863 of SPS

The cooling circuits SF1 and 863 were chosen for this campaign for the following reasons:

- There were problems in the past concerning Legionella contamination in the cooling circuits which lead to an increase on the quantities of chemical products used for treatment. These two circuits have the most intense treatments;
- There were 5 preventive shock treatments scheduled for these two points at already defined times;
- These two cooling circuits represent the two biggest cooling circuits of the two most important accelerators at CERN, the LHC and the SPS;
- The biocide treatment input procedures differs, varying between automatic (according to the level of residual chlorine) at building 863 and periodic at SF1.

RAMSES Point PA1

RAMSES initials stand for RAdiation Monitoring System for the Environment and Safety. It is a project for implementing at CERN, a state-of-the-art radiation monitoring and alarming system, for the Large Hadron Collider (LHC) including about 350 monitors both in the LHC underground areas and on the surface inside and outside of CERN perimeter. RAMSES monitors not only radiation but also the releases of air and water into the environment from the LHC installations, regarding conventional environmental parameters such as physico-chemical parameters.

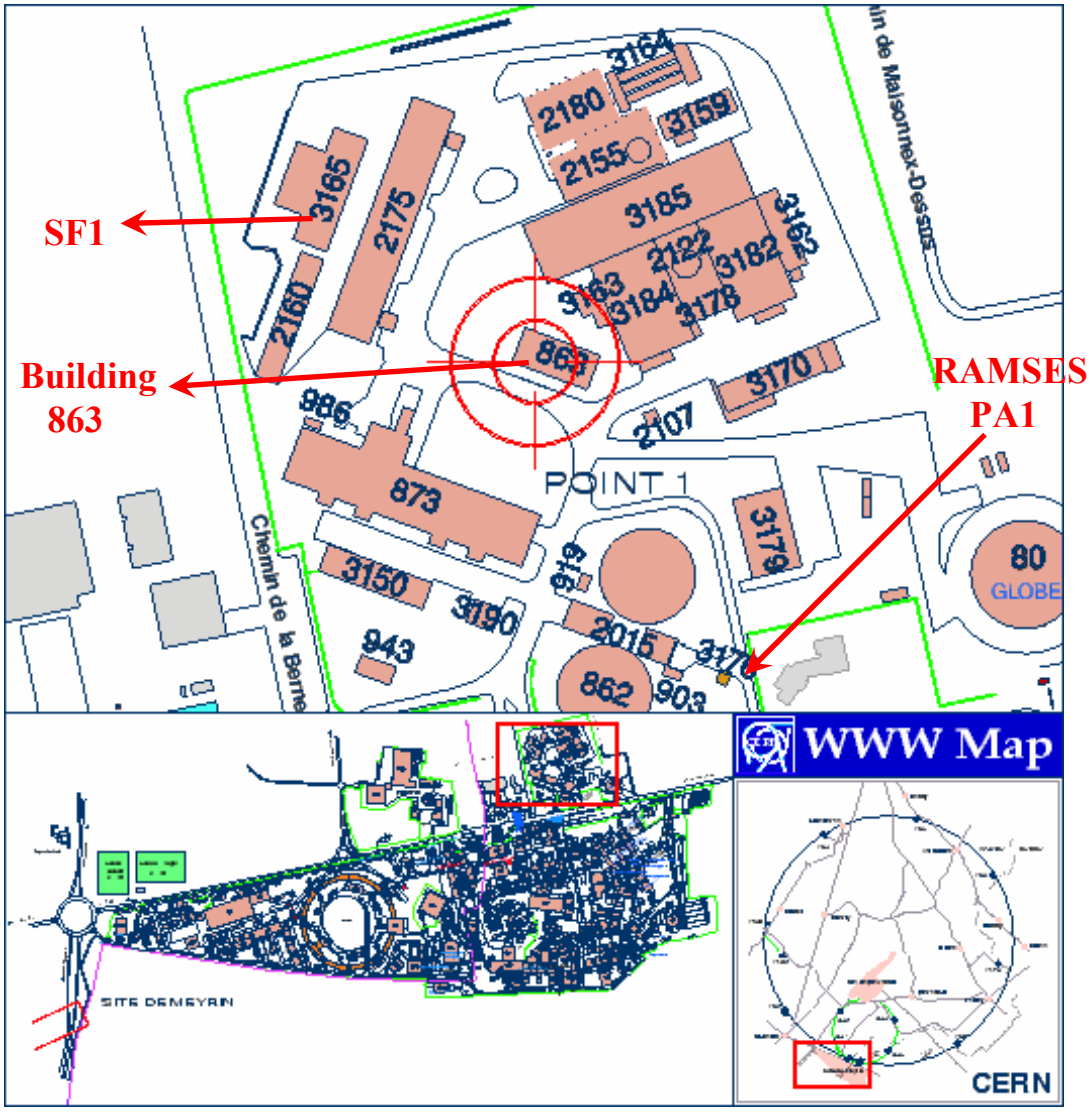
Within the 350 monitors of RAMSES spread out in different locations throughout CERN, point PA1 was selected because this point oversees the water that will be discharged from all open and semi-closed cooling systems of the LHC and SPS, as well as the infiltration water of the tunnels and meteoric water. This way, it was expected to obtain a result that would show the impact of the discharges from the cooling circuits SF1 and building 863 on the overall quality of CERN's major effluent that is released towards this point before reaching the river Nant d'Avril.

9.1.1 General Description of measuring points

The knowledge of the characteristics of the measuring points was important to establish a sampling protocol concerning aspects such as procedure for taking the samples, time and duration of sampling.

9.1.1.1 Location of the selected points

The following figures show a map with the locations where the sampling campaigns were preformed within CERN.



9.1.1.2 LHC cooling circuit point SF1

As mentioned before, the LHC has 8 surface points spread out on the ground above the tunnels. Within those 8 points, there are 5 points that hold water systems. The semi-closed cooling circuit SF1 is one of those points.

Figure XVII shows the outside appearance of point SF1 and the four cooling towers through were water vapour is released into the air.

Figure XVII – Outside view of SF1 and its four cooling towers

As shown above, SF1 has four cooling towers of the 32 existent within the LHC water cooling system. The circuits that pass through the towers shown in Figure XVII hold a total water volume of 1500 m^3, making this way, SF1's cooling circuits to represent 30% of the total volume of water in the LHC cooling circuits and 13% of the total volume of all CERN's semi-closed cooling circuits.

The average flow rate at SF1 is 3440m^3/h and it is one the biggest from all the LHC circuits.

There are two circuits being cooled down at SF1:

- BA6 circuit that is 30 years old;
- SUX1 that is 15 years old;

The temperature differential within SF1 circuits is 24 to 34. This means that, in average, the water from the primary circuit comes in at 34 ºC after refrigerating the secondary circuit and is then cooled down to 24 ºC, loosing 10 ºC in the process.

As a result of all this facts, the cooling power at SF1 is 40 MW out of 294 in the whole LHC water cooling system.

9.1.1.3 SPS cooling circuit Building 863

The cooling circuit at building 863 is semi-closed and holds 4 out of the 11 cooling towers of the SPS water cooling system.

Building 863 handles a volume of water of 4000 m^3 which represents 72% of the total volume of the SPS water cooling system and 36% of the whole semi-closed cooling circuits of CERN. Its flow is 3600 m^3/h and it is the highest at the SPS.

The volume and flow rate of the semi-closed cooling circuits at building 863 together with the circuit design make this circuit present the biggest cooling power of all of CERN circuits. This power is 70 MW and it stands for 50% of the whole cooling power of the SPS water cooling system. At building 863, the temperature of the water cooled at this circuit is lowered from 36 ºC to 26 ºC losing 10ºC in the process.

Figure XVIII – External aspect of building 863 and the globe of innovation

9.1.1.4 RAMSES point PA1

RAMSES point PA1 is equipped with monitors that work in continuous analysing parameters such as:

- Radiation;
- Conventional Environmental Parameters on water quality :
  - pH;
  - Conductivity;
  - Dissolved O_2;
  - Temperature.
- Discharge Parameters:
  - Flow rate.

Unfortunately, at the time of the sampling campaigns the RAMSES system was not fully operational.

Figure XIX – RAMSES point PA1 measuring station

9.1.2 Treatments at building 863 and at SF1

Once this work focuses on the impact of the water treatments done at CERN, it is vital to proceed with a detailed analysis of the treatments done at the specific sampling campaign measuring points.

This way, it is hereby detailed the treatment applied in both selected points of the semi-closed cooling circuits of CERN making the division between Regular and Shock treatment as explained before.

9.1.2.1 Regular Treatment

Anti-Corrosion and Anti-Scaling product

The input of the anti-corrosion and the anti-scaling product is done in a continuous way over time for both of the cooling circuits of the present study, Building 863 and SF1.

Regular biocide

The regular biocide input procedure varies between Building 863 and SF1:

- For Building 863, the input is automatic and controlled by a machine, generally called Trasar that measures the concentration of residual chlorine in the water and inserts the product according to this value. This machine keeps the concentration of residual chlorine in the water above a level of 0,5 ppm.

- For SF1, at the time of the sampling campaigns the input was done in a punctual way, on Wednesdays and Fridays at 8h30. However, this procedure input is scheduled to change, as the Trasar unit will start to work also at SF1, until the end of the year 2007.
  Nonetheless, at the time when the sampling campaigns were conducted, this product was being inserted in the circuit manually and directly on the injection basin at the cooling tower from there it was spreading to the rest of the cooling circuit.

9.1.2.2 Shock Treatment

Specific *Legionella* Biocide

Varying accordingly to the conditions described in chapter 7 and with the supervision of CERN's TS-CV department, NALCO makes shock treatments inserting in the cooling circuits specific *Legionella* Biocide by manual means.

Both at SF1 and at building 863, the product insertion point is the injection basin of the cooling tower and from there the flow of the cooling circuit makes the product spread to the rest of the cooling circuit, thus reducing the concentration of the *Legionella* bacteria and other microorganisms.

Biodetergent

Both in Building 863 and point SF1, biodetergent is only inserted during shock treatments.

Biodetergent is inserted simultaneously with the specific *Legionella* product and the input procedure is the same as above described for specific *Legionella* product.
As the ratio between the specific *Legionella* biocide and Biodetergent is fixed, the quantity of Biodetergent inserted is always equal to 10% of the total quantity of the specific *Legionella* treatment.

9.1.2.3 Overview of treatment procedure at SF1 and building 863

The following table shows the input procedure in the selected measuring points where treatment is done. The input procedure is divided according to the different products used.

Table 24 – Type of product input at 863 and SF1

Product	Building 863	SF1
Anti Corrosion, Anti Scaling	Continuous	Continuous
Biocide	Continuous	Continuous after the 2007 but punctual at the time of the campaign
Specific *Legionella* Biocide	Punctual	Punctual
Biodetergent	Punctual	Punctual

9.1.2.4 Quantities of product used in the treatments done at SF1 and building 863 in 2007

During the year of 2007, SF1 and at Building 863 had an equal number of *Legionella* shock treatments performed. In each location, there were 7 treatments done, being that 1 treatment was corrective and the 6 were preventive. The following table contains the times of these treatments:

Table 25 – Times and types of treatments at SF1 and Building 863 during 2007

Type of treatment	Building 863	SF1
Corrective	21/5	10/5
Scheduled Preventive	18/6	18/6
Scheduled Preventive	24/07	24/07
Scheduled Preventive	21/08	21/08
Scheduled Preventive	18/9	18/9
Scheduled Preventive	18/10	18/10
Cleaning of circuits (Preventive)	04/01/2008	04/01/2008

Having in mind that 7 treatments were done and that each treatment performed at SF1 and Building 863 uses a quantity of specific *Legionella* Biocide (in kilos) that is equal to 10% of the total volume of the circuit (in m^3), the total amount of specific *Legionella* biocide inserted in both building 863 and SF1 during the year 2007 can be calculated.

Table 26 – Calculus of the quantity of *Legionella* biocide used in 2007 in SF1 and building 863

Location	Number of treatments	Volume of circuit (m^3)	Quantity input per treatment (Kg)	Total quantity (Kg)
Building 863	7	4000	400	2800
SF1	7	1500	150	1050

The quantity of biodetergent inserted was 10% of the value presented in previous table. The previous table shows the total quantities of all products that were inserted in building 863 and SF1 during the year of 2007.

Table 27 – Product quantities inserted at SF1 and building 863 during the year of 2007

Product	Building 863	SF1
Regular Biocide	1700 kg	410 kg
Anti-scaling and Anti Corrosion	3340 l	1365 l
Specific *Legionella* Biocide	2800 kg	1050 kg
Biodetergent	280 kg	105 kg

9.1.3 Description of discharges at SF1 and building 863

The knowledge of the discharges both at SF1 and building 863 was vital for the success of the sampling campaign once it was important to take samples that would contain the highest concentrations of the products used for treatments in order to measure in a worst case scenario.

9.1.3.1 LHC cooling circuit point SF1

The total amount of water that is released in SF1 is in average 1000 m^3/week. This is an average done in one full year, considering both summer (bigger water consumption and discharge) and winter (small water consumption and discharge).

However, both the quantity and time of the discharges, is varying considerably depending on a large number of parameters such as:

- Weather conditions such as air temperature or air moisture;
- LHC functioning and need for cooling.

This way, SF1 records quite different releases according to the week in question. As an example, on week 15 of the year 2007, the release amounted to 1785 m^3/week but on week 20 of the same year, the water discharged was around 658 m^3/week.

At SF1 there are 4 types of reject:

- De-concentration;
- Circuit filters;
- Sand filters;
- Water coming from the reject basin.

De-concentration water

De-concentration water is normal water from the circuits that has reached a conductivity superior to 850 µS/cm. This water is discharged so that make-up water can go into the cooling circuit in order to dilute the water inside the cooling circuit that due to evaporation has an increased value of conductivity. Without this procedure the water inside the cooling circuit would not present the optimal conditions and could exhibit high corrosiveness or other undesired proprieties.

The sole criterion for doing a de-concentration operation is conductivity. Whenever the conductivity of the water inside the circuit reaches 850 µS/cm, de-concentration water is discharged. This way, the discharges from de-concentration water are never at a fixed time. However, it can be said that in average, there are 3 de-concentration operations per day each lasting around 25 minutes and spending an approximated volume of water of 37,5 m^3. After 6 days, this accounts for an averaged volume of 675 m^3.

Circuit filters

There are two circuit filters at SF1. One is for the circuit SUX1 and another for the circuit BA6. These small filters serve purposes of cleaning the water.

These filters are periodically rinsed with a water flow in the opposite direction of normal. This is done to remove the particles retained in the filters in order to increase the efficiency of the filters. This procedure is done 12 times a day. Each time a filter is cleaned, a water flow of 12 m^3 is discharged

Sand filter

The sand filter is the big filter of the circuit. This filter serves to remove small pebbles and other impurities from the cooling circuits in order to avoid water contamination and problems with the optimal functioning of the circuits.

The sand filter is cleaned once in every 144 hours which is equivalent to 6 days. This filter is cleaned by means of automatic taps that reverse the flow in the section that contains the filter. Then, cooling water flows through the filter rinsing it. In average, a volume of 30 m^3 is discharged every time the filter is cleaned. This procedure is done to remove the particles retained in the filters with the goal of increasing the efficiency of the filters.

Water coming from the reject basin

In very rare situations such as cleaning operations or yearly maintenance, water may flow to the reject basin that is located in the basement of SF1. The water discharged in this way is quite small in volume and it was considered to be insignificant by comparison with the volume the other rejects.

Overview of the reject at point SF1

According to data supply by TS-CV, in the year 2007, the total water consumed at SF1 was 97858 m^3 and the total water discharged was 21831 m^3.

Regarding the year of 2004, the annual consumption of water was 36547 m^3. This includes the estimated evaporated water that was 24365 m^3 and the discharged water that was 12182 m^3.

An important aspect to bear in mind is that the final release from SF1 (before the discharge water exits the building) is ultimately controlled by a switch. During shock treatments, this switch is forced to the position off for 6 hours so that there are no releases and product has time to act.

The following table shows an average of the water volumes discharged and its characteristics divided per type of reject and per discharge.

Table 28 – Average of the water volume discharged at SF1 divided per types of reject and per discharge [14]

Type of Reject	Per discharge					Per discharge with all filters
	Number of filters	Duration (minutes)	Duration (hours)	Average flow (m^3/h)	Volume of water discharged (m^3)	Total volume discharged (m^3)
De-concentracion	1	25	0,42	90	37,5	37,5
Sand	1	20	0,34	90	30	30
Circuit Filters	2	2	0,03	185	6,2	12,3

The following table shows the same average in water volumes discharged and its characteristics divided per type of reject and per 6 days, allowing an overall view on the relevance of each type of reject to the total discharged volume.

Table 29 - Water volume discharged at SF1 divided per types of reject and per 6 days[15]

Type of Reject	Per day		Per 6 days	
	Number of discharges	Total volume discharged (m^3)	Number of working times	Total volume discharged (m^3)
De-concentracion	3	112,5	18	675
Sand	0,2	5	1	30
Circuit Filters	12	148	72	888

This way, a theoretical total volume of water of 1593 m^3 is discharged from SF1 every six days.

After each sampling campaign was carried out, a graphic was made that comprised several days of discharges made from SF1. The analyses of these graphic allowed for a better understanding of what was being sample. These graphics are present in annex 7.

9.1.3.2 SPS cooling circuit building 863

De-concentration water in building 863 is discharged according to the same criteria than for SF1. The SPS cooling circuit of building 863 is also equipped with circuit filters and a sand filter that work under the same guidelines as SF1.

The final release from building 863 (just before exiting the building) is also ultimately controlled by a switch. Just as for SF1, during shock treatments, this switch is also forced to the position off for 6 hours so that there are no releases and product has time to act. Further information about the amount of water discharged by building 863 was not available for the year of 2007.

The water consumption in the year of 2007 at this location was 179487 m^3. In the year of 2004, the annual consumption of water was 207862 m^3. This includes the estimated evaporated water that was 138575 m^3 and the discharged water that was 61977 m^3.

[14] According to values given by TS-CV group
[15] According to values given by TS-CV group

9.2 Selection of parameters to measure

This chapter deals with the selection of parameters for the measurements as well as the choice of laboratory to perform the analyses and the norms used in the test.

9.2.1 Definition of a list of parameters

The following table presents a list of parameters that are currently measured at CERN's effluent and their possible origins:

Table 30 - Parameters measured in CERN effluents and their possible sources

Parameter	Possible pollution source at CERN
Temperature	Discharge of cooling water
pH	Accidental leakage of acids or bases
Conductivity	Industrial activities and installations, leakage of demineralised water
Dissolved oxygen	Leakage of sanitary sewage, water treatment
Turbidity	Leakage of sanitary sewage, civil engineering
Suspended matter	Leakage of sanitary sewage, civil engineering
BOD_5 (Biochemical oxygen demand after 5 days)	Leakage of sanitary sewage water or biodegradable (in)-organic substances
COD (Chemical oxygen demand)	Leakage of sanitary sewage water or non-biodegradable (in)-organic substances
DOC (Dissolved organic carbon)	Leakage of sanitary sewage water, water treatment in cooling circuits
Ammonium	Leakage of sanitary sewage water
Nitrites	Leakage of sanitary sewage water, water treatment
Nitrates	Water treatment
Chlorides	Water treatment
Copper	Electroplating, corrosion of cooling circuits
Zinc	Water treatment, electroplating
Iron	Welding, corrosion of cooling circuits
Aluminium	Corrosion of cooling circuits
Lead	Welding
Zinc	Water treatment
Hexavalent Chromium (Cr^{VI})	Electroplating
Cadmium	Use of batteries
Nickel	Electroplating
Cyanides	Electroplating
Adsorbable organic halogens (AOX)	Water treatment, chemical degreasing
Total hydrocarbons	Miscellaneous industrial activities and installations

The previously presented table was taken into account while establishing the list of parameters to be analysed in the sampling campaigns. Despite this the main factor for this decision draw upon a cross check of the applicable regulations with the products used for water treatments and other possible water pollutants sources.

The list of parameters to be analysed in the sampling campaigns was established through cross checking the regulations with the products used for water treatments and other possible water pollutants sources.

This way, the initial list of the parameters to measure was extensive, holding a total of 26 parameters, as shown bellow:

Basic Physico-Chemical Parameters:

- pH;
- Conductivity;
- Temperature;
- Suspended matter.

Organical Parameters:

- DOC - Dissolved Organic Carbon < 0.45 μm;
- BDO_5 - Biological Demand for Oxygen;
- CDO - Chemical Demand for Oxygen;
- AOX after filtration - Adsorbable Organic Halides.[16]

Metals:

- Total Aluminium
- Total Arsenic
- Total Chrome
- Hexavalent Chrome (Cr^{VI})
- Total Iron
- Total Cadmium
- Total Copper
- Total Zinc
- Total Cobalt
- Total Nickel
- Total Lead
- Total Tin

[16] This parameter is further discussed in annexes 2 and 3

Disinfection Parameters:

- Brome
- Free Chlorine [17]

Others:

- Ammonium
- Nitrates
- Nitrites
- Total Cyanides

In annex, further data on specific parameters such as AOX and Chlorine is analysed.

9.2.2 Choice of laboratory for sampling campaign

The choice of laboratory for the campaign was based on the combination of the criteria bellow described:

- **Distance** from laboratory to CERN, once the samples had to arrive without significant alteration so that result would be correct;
- **Credibility** of laboratory to insure that results are reliable;
- **Cost** once the section budget for the analyses was limited and it was intended to conduct a minimal of two campaigns on the three above mentioned points.

After pondering all these aspects the decision was taken in favour of the laboratory "CARSO - LSEHL, Laboratoire Sante Environnement Hygiene". This laboratory was located in Lyon which is at a distance of 146 kilometres from CERN, corresponding to approximately two hours of travel. Samples were maintained under controlled condition as described in next chapter.

However, not all samples were sent to CARSO, some samples were analyzed by staff member of CERN's SC-IE environmental section, at the CERN environmental laboratory, thus providing a comparison value.

It should be noted that the following parameters were analyzed by CERN:

- Temperature
- pH
- Conductivity
- Dissolved O2

[17] This parameter is further discussed in annexes 4 and 5

9.2.3 Norms used on the analyses by chosen laboratories

The following two tables show the methods, norms and whether the test used were credited by COFRAC (Comité Français d'Accréditation (France)).

The first table concerns the tests done by CARSO laboratories when analyzing the samples provided by CERN:

Table 31 – Method, norms and COFRAC accreditation used by CARSO

Parameter	Unit	Method	Norm	COFRAC Accreditation
Suspended matter	mg/l	Gravimetry after filtration	NF EN 872	Yes
DOC (Dissolved organic carbon)	mg/l C	Oxidation through wet way and IR	NF EN 1484	Yes
BOD_5 (Biochemical oxygen demand after 5 days)	mg/l O_2	Without dilution	NF EN 1899-2	Yes
COD (Chemical oxygen demand)	mgl/ O_2	Potentiometry	NF T90-101	Yes
Hexavalent Chromium (Cr^{VI})	mg/l Cr^{VI}	Spectrophometry	NF T90-043	-
Cyanides	mg/l CN^-	Continuous Flux (CFA)	NF EN ISO 14403	-
AOX (Adsorbable organic halogens)	mg/l Cl	Couloremetry after filtration	NF EN ISO 9562	Yes
Bromine	mg/l Br_2	Spectrophometry with DPD	Internal Method	-
Free Chlorine	mg/l Cl_2	Spectrophometry with DPD	NF EN ISO 7393-2	-
Ammonium	mg/l NH^{4+}	Spectrophometry with blue of indophenol	NF T90-015-2	Yes
Nitrates	mg/l NO^{3-}	Ionic Chromatografy	NF EN ISO 10304-1	Yes
Nitrites	mg/l NO^{2-}	Spectrophometry	NF EN 26777	Yes
Total Aluminium	mg/l Al	ICP/MS after acidification and decantation	ISO 17294 – 1 and 2	Yes
Total Arsenic	mg/l As	ICP/MS after acidification and decantation	ISO 17294 – 1 and 2	Yes
Total Chrome	mg/l Cr	ICP/MS after acidification and decantation	ISO 17294 – 1 and 2	Yes
Total Iron	mg/l Fe	ICP/MS after acidification and decantation	ISO 17294 – 1 and 2	-
Total Cadmium	mg/l	ICP/MS after acidification and decantation	ISO 17294 – 1 and 2	Yes
Total Copper	mg/l	ICP/MS after acidification and decantation	ISO 17294 – 1 and 2	Yes
Total Zinc	mg/l	ICP/MS after acidification and decantation	ISO 17294 – 1 and 2	Yes
Total Cobalt	mg/l	ICP/MS after acidification and decantation	ISO 17294 – 1 and 2	Yes
Total Nickel	mg/l	ICP/MS after acidification and decantation	ISO 17294 – 1 and 2	Yes
Total Lead	mg/l	ICP/MS after acidification and decantation	ISO 17294 – 1 and 2	Yes
Total Tin	mg/l	ICP/MS after acidification and decantation	ISO 17294 – 1 and 2	Yes

This table concerns the methods of the tests done by CERN's environmental laboratory:

Table 32 - Method and measuring range used by CERN's environmental laboratory

Parameter	Unit	Method	Measuring Range
DOC (Dissolved organic carbon)	mg/l C	Filtration of the water sample (0.45 µm), dissolved organic carbon is measured by using the combustion catalytic oxidation/NDIR method.	0.05 – 25000 mg/l C
COD (Chemical oxygen demand)	mgl/ O_2	Photometric determination of decrease in chromate concentration after two hours and oxidation with potassium dichromate / sulphuric acid / silver sulphate at 148°C.	2 – 40 mg/l O_2 15 – 160 mg/l O_2 50 – 300 mg/l O_2 100 – 1500 mg/l O_2
AOX (Adsorbable organic halogens)	mg/l Cl	Solid phase extraction with an adsorbing cartridge, decomposition of the enriched adsorber (removal of the inorganic chloride), determination as chloride with mercury thiocyanate.	0.01 – 3 mg/l AOX
Total Chlorine and Free Chlorine	mg/L Cl^-	Photometric determination with mercury (II) thiocyanate and iron (III) nitrate.	0.5 – 50 mg/l Cl^-
Total Zinc	mg/l	Photometric determination with zincon.	0.1 – 4 mg/l Zn^{2+}

9.3 Sampling Plan

According to the objectives establish for this work, a sampling plan was elaborated.

9.3.1 Definition of schedule

It was decided to firstly make two sampling campaigns on the reject waters of SF1, building 863 and RAMSES PA1 during two scheduled preventive shock treatment in order to obtain a sample with high concentration of the product used against *Legionella*.

After analyzing the obtained results, two further sampling campaigns were done during regular treatment in specific measuring points.

Sampling during both regular and shock treatments was intended to show us the difference between both situations, always bearing in my mind that shock treatment is cumulative with the regular treatment.

Sampling was not conducted the in the worst case scenario for the shock treatments (this would correspond to acute shock treatments in which an insertion of *Legionella* specific biocide in a concentration of 200 ppm and biodetergent is done along side with regular treatment) because it is unpredictable when such a situation will occur and if it is going to occur.

The following table shows a summarization of the times of sampling and the correspondent treatment sorted by measuring point:

Table 33 – Type of treatment per campaign per measuring point

Measuring point	Campaign			
	First	Second	Third	Fourth
SF1	Scheduled Preventive Shock Treatment	Scheduled Preventive Shock Treatment	Regular Treatment	Regular Treatment
Building 863	Scheduled Preventive Shock Treatment	Scheduled Preventive Shock Treatment	Regular Treatment	Not Tested
RAMSES PA1	Scheduled Preventive Shock Treatment	Scheduled Preventive Shock Treatment	Not Tested	Not Tested

Next table shows us the dates and times of sampling and the number of samples collected divided per sampling campaign:

Table 34 – Schedule of the sampling campaigns

Campaign			SF1	Building 863	RAMSES PA1
Campaign	First	Day	19/06/2007		
		Number of samples	2	2	1
		Time	14h12 to19h12 19h12 to 00h12	16h15 18h15	16h20
	Second	Day	24/07/2007		
		Number of samples	3	1	1
		Time	14h30 to 20h30 20h30 to 02h30 15h30	15h45	16h00
	Third	Day	18/09/2007		-
		Number of samples	1	1	0
		Time	17h00	17h10	-
	Fourth	Day	04/10/2007	-	-
		Number of samples	5	0	0
		Time	07h30 (twice) 10h00 11h40 (twice)	-	-

The times shown above were chosen not only considering the time of the preventive shock treatment abut also having also in mind that the valve would be closed for 6 hours after the time of the treatment. It was intended that the sample would be representative of the moment when the products used in the shock treatment were present in the release at maximum concentration.

It was considered that the products from regular treatment would always be present in approximately the same concentrations no matter when the sample was being taken.

9.3.2 Evaluation of parameters per campaign

On the four sampling campaigns conducted, two types of checks were done:

- Full parameter Check;
- Specific parameter Check;

The full parameter check was used in the two initial campaigns.

The full parameter check had a broad objective, intended for an overall detection of pollutants. This way, the list of the parameters for these first two campaigns was extensive, holding a total of 26 parameters.

A specific parameter check was used for the two other campaigns.

These campaigns were done only in specific parameters whose values were though to be more problematic after the analyses of the results of the previous sampling campaigns. Those parameters were as listed below:

- DOC;
- Free chlorine;
- Total chlorine; (only on third campaign)
- AOX;
- COD;
- Zinc.

Also other basic parameters were checked such as temperature, pH and conductivity.

On third campaign both free chlorine and total chlorine parameters were checked. However, on the fourth campaign, only the free chlorine was checked. This parameter is more relevant because legislation makes use of this parameter. Total chlorine was checked with comparison purposes.

The table bellow presents a small overview of the types of parameter chosen distributed per campaign and per measuring point:

Table 35 – Campaign goals

Place	Campaign			
	First	Second	Third	Fourth
SF1	Full parameter Check	Full parameter Check	Specific parameter Check	Specific parameter Check
Building 863	Full parameter Check	Full parameter Check	Specific parameter Check	Specific parameter Check
RAMSES PA1	Full parameter Check	Full parameter Check	Specific parameter Check	Specific parameter Check

9.3.3 Laboratory performing the analyses

The following table shows an overview of the laboratories where the samples were analysed for each of the sampling campaigns:

Table 36 - Laboratories per sampling campaign

Place	Campaign			
	First	Second	Third	Fourth
SF1	CARSO	CARSO	CERN's Environmental Laboratory	CARSO & CERN's Environmental Laboratory
Building 863	CARSO	CARSO	CERN's Environmental Laboratory	CARSO & CERN's Environmental Laboratory
RAMSES PA1	CARSO	CARSO	CERN's Environmental Laboratory	CARSO & CERN's Environmental Laboratory

9.3.4 Sample handling

In order to minimize the risks of interference in the results, it was discussed with CARSO Laboratory a procedure for maintaining the samples in its initial status. This procedure is described bellow:

- Samples were kept in a cooler box with ice elements in order to maintain a low temperature that inhibits bacterial actions. In addition, (once samples had to be kept overnight due to the impossibility of sending the samples to CARSO in the day of sampling) samples were maintain in refrigerator to avoid unwanted reactions that would alter initial parameters;
- Glass containers were used because plastic containers were inappropriate for some of the analyses that were done, for example for the AOX parameter plastic containers may alter the result;
- Samples were delivered personally to CARSO.

Samples analyzed by CERN's environmental laboratory were conducted straight away in order to minimize the risks of interference.

9.3.5 Sampling place & equipment used

According to the specific characteristics of each measuring point, the sampling place was always chosen in order to obtain a result that would include the entire reject and the time when the reject would possibly exhibit the worst characteristics.

The following table shows the location where the samples were taken at each sampling point:

Table 37 – Place of measure and type of effluent measured

Measuring Point	Campaign			
	First	Second	Third	Fourth
SF1	Water from Circuits	Water from Circuits	De-concentration water collected at the manhole outside SF1	De-concentration water collected at the manhole outside SF1
Building 863	Water from Circuits	Water from Circuits	Release of de-concentration water outside Building 863	Not tested
RAMSES PA1	Global effluents from the site collected at PA1 of RAMSES (doesn't include the de-concentration from SF1 and building 863)	Global effluents from the site collected at PA1 of RAMSES (includes the de-concentration from SF1 and building 863)	Not tested	Not tested

All samples taken at building 863 and at RAMSES PA1 were done in a punctual way.
Samples taken at SF1 were done in a combined way for the first two sampling campaign and in a punctual way. The combined samples were taken by a machine named ISCO. This machine is a sampler that was programmed to work from 14h12 to 00h12 in the first sampling campaign and from 14h30 to 02h30 in the second sampling campaign. Each hour the sample took a fix amount of water from the reject water at

SF1. In the first sampling campaign, the machine was programmed to take 1000 ml of sample per hour and in the second 800 ml per hour. After, these hourly samples were mixed to form a combined sample that would be more representative. In the first sampling campaign 5 hourly samples were combined and in the second campaign 6 hourly samples were combined.

9.3.6 Overview of sampling campaign protocol

The following tables present an overview of the sampling protocol divided by campaigns.

Table 38 – Overview of the first campaign

First Sampling Campaign (19 of June of 2007)			
Point of Measure	**SF1**	**863**	**RAMSES**
Number of samples taken	2	2	1
Time	From 14h12 to 19h12 From 19h12 to 00h12	At 16h15 At 18h15	At 16h20
Type of sampling	Combined	Punctual	Punctual
Location	Inside the Circuit	Inside the Circuit	Manhole outside PA1
Parameter Measured	Full parameter Check	Full parameter Check	Full parameter Check
Type of treatment	Preventive Shock Treatment	Preventive Shock Treatment	Preventive Shock Treatment
Analyser	CARSO	CARSO	CARSO

Table 39 - Overview of the second campaign

Second Sampling Campaign (24 of July of 2007)			
Point of Measure	**SF1**	**863**	**RAMSES**
Number of samples taken	3	1	1
Time	From 14h30 to 20h30 From 20h30 to 02h30	At 15h30 At 15h45	At 16h00
Type of sampling	Combined	Punctual	Punctual
Location	Inside the Circuit	Inside the Circuit	Manhole outside PA1
Parameter Measured	Full parameter Check	Full parameter Check	Full parameter Check
Type of treatment	Preventive Shock Treatment	Preventive Shock Treatment	Preventive Shock Treatment
Analyser	CARSO	CARSO	CARSO

Table 40 - Overview of the third campaign

Third Sampling Campaign (18 of September of 2007)			
Point of Measure	**SF1**	**863**	**RAMSES**
Number of samples taken	1	1	0
Time	17h	17h10	-
Type of sampling	Punctual	Punctual	-
Location	Manhole outside SF1	Manhole outside building 863	-
Parameter Measured	Specific parameter Check	Specific parameter Check	-
Type of treatment	Regular Treatment	Regular Treatment	-
Analyser	CERN's Environmental Laboratory	CERN's Environmental Laboratory	-

Table 41 - Overview of the fourth campaign

Fourth Sampling Campaign (4 of October of 2007)			
Point of Measure	**SF1**	**863**	**RAMSES**
Number of samples taken	5	0	0
Time	07h30 (2 samples) 10h00 11h40 (2 samples)	-	-
Type of sampling	Punctual	-	-
Location	Manhole outside SF1	-	-
Parameter Measured	Specific parameter Check	-	-
Type of treatment	Regular Treatment	-	-
Analyser	CARSO & CERN's Environmental Laboratory	-	-

10 PRESENTATION OF RESULTS

The results obtained in the sampling campaigns are here presented in the form of table. Results are grouped per sampling campaign.

The numbers marked in bold are values that were considered to be of some concern because values are higher than the limits or approaching the limits.

It is also important to notice that the 5 first parameters of the 1º and 2 º campaigns were measured in situ by CERN.

1º Campaign

Day: 19 of June of 2007

Table 42 – Overview of the results of the first sampling campaign

First Sampling Campaign (19 of June of 2007)						
Point of Measure	**Unit**	**SF1 nº1** (14h12 to 19h12)	**SF1 nº2** (19h12 to 00h12)	**Building 863 nº1** (16h15)	**Building 863 nº2** (18h15)	**Ramses** (16h20)
Temperature	ºC	-	-	12.7	13.5	13.3
pH	-	-	-	-	-	-
Conductivity	µS/cm	730	720	655	660	586
Dissolved O_2	mg/L	-	-	-	-	-
Turbidity	NTU	-	-	-	-	-
Suspended matter	mg/l	**2.2**	< 2.0	< 2.0	< 2.0	< 2.0
DOC (Dissolved organic carbon)	mg/l C	**14**	**8.6**	**9.5**	7.1	3.4
BOD_5 (Biochemical oxygen demand after 5 days)	mg/l O_2	1.3	< 0.5	< 0.5	< 0.5	0.5
COD (Chemical oxygen demand)	mgl/ O_2	**56**	**33**	25	24	< 20.0
Hexavalent Chromium (Cr^{VI})	mg/l Cr^{VI}	< 0.010	< 0.010	< 0.010	< 0.010	< 0.010
Cyanides	mg/l CN^-	< 0.010	< 0.010	< 0.010	< 0.010	< 0.010
AOX (Adsorbable organic halogens)	mg/l Cl	**0.17**	**0.11**	**0.24**	**0.19**	< 0.05
Bromine	mg/l Br_2	**1.19**	**1.14**	**5.40**	**5.05**	0.42
Free Chlorine	mg/l Cl_2	0.07	0.07	**1.42**	**1.31**	0.06
Ammonium	mg/l NH^{4+}	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05
Nitrates	mg/l NO^{3-}	10.8	10.4	8.9	8.3	6.8
Nitrites	mg/l NO^{2-}	0.02	0.02	< 0.02	< 0.02	< 0.02
Total Aluminium	mg/l Al	**0.018**	**0.015**	**0.016**	**0.021**	**0.034**
Total Arsenic	mg/l As	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005
Total Chrome	mg/l Cr	< 0.010	< 0.010	< 0.010	< 0.010	< 0.010
Total Iron	mg/l Fe	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05
Total Cadmium	mg/l	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001
Total Copper	mg/l	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05
Total Zinc	mg/l	**0.43**	**0.46**	**0.64**	**0.62**	0.26
Total Cobalt	mg/l	< 0.010	< 0.010	< 0.010	< 0.010	< 0.010
Total Nickel	mg/l	< 0.010	< 0.010	< 0.010	< 0.010	< 0.010
Total Lead	mg/l	< 0.010	< 0.010	< 0.010	< 0.010	< 0.010
Total Tin	mg/l	< 0.010	< 0.010	< 0.010	< 0.010	< 0.010

2º Campaign

Day: 24 of July of 2007

Table 43 - Overview of the results of the second sampling campaign

Second Sampling Campaign (24 of July of 2007)						
Point of Measure	**Unit**	**SF1 nº1** (14h30 to 20h30)	**SF1 nº2** (20h30 to 02h30)	**SF1 nº3** (15h30)	**Bulding 863 nº1** (15h45)	**Ramses** (16h00)
Temperature	ºC	24	24	29	24	**24.4**
pH	-	8.75	8.7	8.65	8.7	8.8
Conductivity	µS/cm	750	750	750	870	678
Dissolved O_2	mg/L	-	-	-	-	-
Turbidity	NTU	-	-	-	-	-
Suspended matter	mg/l	< 2.0	< 2.0	< 2.0	**10**	**2.8**
DOC (Dissolved organic carbon)	mg/l C	**10**	**8.0**	**7.8**	6.7	6.8
BOD_5 (Biochemical oxygen demand after 5 days)	mg/l O_2	1.0	< 0.5	< 0.5	< 0.5	< 0.5
COD (Chemical oxygen demand)	mgl/ O_2	**46**	24	33	< 20.0	**41**
Hexavalent Chromium (Cr^{VI})	mg/l Cr^{VI}	< 0.010	< 0.010	< 0.010	< 0.010	< 0.010
Cyanides	mg/l CN^-	< 0.010	< 0.010	< 0.010	< 0.010	< 0.010
AOX (Adsorbable Organic Halogens)	mg/l Cl	**0.10**	**0.11**	**0.10**	**0.12**	**0.05**
Bromine	mg/l Br_2	**0.24**	**0.60**	**0.85**	**1.6**	**0.67**
Free Chlorine	mg/l Cl_2	**0.07**	< 0.05	< 0.05	**0.15**	< 0.05
Ammonium	mg/l NH^{4+}	< 0.05	<0.05	<0.05	<0.05	<0.05
Nitrates	mg/l NO^{3-}	10.3	10.1	10.5	9.5	9.1
Nitrites	mg/l NO^{2-}	0.04	0.04	0.04	< 0.02	0.03
Total Aluminium	mg/l Al	**0.011**	< 0.010	< 0.010	< 0.010	**0.021**
Total Arsenic	mg/l As	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005
Total Chrome	mg/l Cr	< 0.010	< 0.010	< 0.010	< 0.010	< 0.010
Total Iron	mg/l Fe	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05
Total Cadmium	mg/l	< 0.001	< 0.001	< 0.001	<0.001	< 0.001
Total Copper	mg/l	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05
Total Zinc	mg/l	**0.42**	**0.42**	**0.47**	**0.40**	**0.36**
Total Cobalt	mg/l	< 0.010	< 0.010	< 0.010	< 0.010	< 0.010
Total Nickel	mg/l	< 0.010	< 0.010	< 0.010	< 0.010	< 0.010
Total Lead	mg/l	< 0.010	< 0.010	< 0.010	< 0.010	< 0.010
Total Tin	mg/l	< 0.010	< 0.010	< 0.010	< 0.010	< 0.010

3º Campaign

Day: 18 of September of 2007

Samples done by CERN's Environmental Laboratory:

Table 44 - Overview of the results of the analyses done by CERN on the third sampling campaign

Third Sampling Campaign (18 of September of 2007)									
Parameter	**DOC** (mg/l C)	**Free Chlorine** (mg/L Cl_2)	**Total Chlorine** (mg/L Cl^-)	**AOX** (after removal of blank 0.7 mg/l Cl^-)	**COD** (mg/ l O_2)	**Zinc** (mg/l)	**pH**	**T** (ºC)	**Conductivity** (µS/cm)
SF1 (17h00)	11.55	< 0.05	0.34	< 0.01	23	< 0.1	8.6	29	759
863 (17h10)	8.8	0.3	1.4	< 0.01	16	0.2	8.8	21	800

4º Campaign

Day: 4 of October of 2007

Samples done by CARSO:

Table 45 - Overview of the results of the analyses done by CARSO on the fourth sampling campaign

Fourth Sampling Campaign (4 of October of 2007)			
Place and time	**Parameter**	**Results**	**Unit**
SF1 (07h30)	**AOX**	0.17	mg/L Cl^-
SF1 (11h40)	**AOX**	0.19	mg/L Cl^-

Samples done by CERN's Environmental Laboratory:

Table 46 - Overview of the results of the analyses done by CERN on the fourth sampling campaign

Fourth Sampling Campaign (4 of October of 2007)									
	DOC (mg/l C)	**Free Chlorine** (mg/L Cl_2)	**AOX** (before removal of blank 0.7 mg/l Cl^-)	**AOX** (after removal of blank 0.7 mg/l Cl^-)	**COD** (mg/ l O_2)	**Zinc** (mg/l)	**pH**	**T** (ºC)	**Conductivity** (µS/cm)
SF1 (07h30)	8.41	0.16	0.9	0.2	15	0.2	8.6	25.6	750
SF1 (10h00)	8.67	0.41	1.2	0.5	20	0.3	8.62	25.0	752
SF1 (11h40 - Purge)	8.67	0.44	1.2	0.5	15	0.2	8.57	25.5	755

In order to be easier for viewing and comparing the information, the following table presents the results of first and second campaign grouped per point of measuring. The most demanding value from the consulted legislation was also included.

Table 47 – Results of first and second sampling campaign grouped per measuring point

Campaign	First		Second			First		Second	First	Second	
Point of Measure	**SF1 nº1** (14h12 to 19h12)	**SF1 nº2** (19h12 to 00h12)	**SF1 nº1** (14h30 to 20h30)	**SF1 nº2** (20h30 to 02h30)	**SF1 nº3** (15h30)	**B. 863 nº1** (16h15)	**B. 863 nº2** (18h15)	**B. 863 nº1** (15h45)	**Ramses** (16h20)	**Ramses** (16h00)	**Limit**
Temperature (ºC)	-	-	24	24	29	-	-	24	-	**24.4**	***30***
pH (Sorensen Scale)	-	-	8.75	8.7	8.65	-	-	8.7	-	8.8	***6.5 to 8.5***
Conductivity (µS/cm)	730	720	750	750	750	655	660	870	586	678	-
Dissolved O_2 (mg/L)	-	-	-	-	-	-	-	-	-	-	-
Turbidity (NTU)	-	-	-	-	-	-	-	-	-	-	-
Suspended matter (mg/l)	**2.2**	< 2.0	< 2.0	< 2.0	< 2.0	< 2.0	< 2.0	**10**	< 2.0	**2.8**	***20***
DOC (mg/l C)	**14**	**8.6**	**10**	**8.0**	**7.8**	**9.5**	7.1	6.7	3.4	6.8	***10***
BOD_5 (mg/l O_2)	1.3	< 0.5	1.0	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	0.5	< 0.5	***20***
COD (mgl/ O_2)	**56**	33	**46**	24	33	25	24	< 20.0	< 20.0	**41**	***40***
Hexavalent Chromium (mg/l Cr^{VI})	< 0.010	< 0.010	< 0.010	< 0.010	< 0.010	< 0.010	< 0.010	< 0.010	< 0.010	< 0.010	***0.1***
Cyanides (mg/l CN^-)	< 0.010	< 0.010	< 0.010	< 0.010	< 0.010	< 0.010	< 0.010	< 0.010	< 0.010	< 0.010	***0.1***
AOX (mg/l Cl^-)	**0.17**	**0.11**	**0.10**	**0.11**	**0.10**	**0.24**	**0.19**	**0.12**	< 0.05	**0.05**	***0.1***
Bromine (mg/l Br_2)	**1.19**	**1.14**	**0.24**	**0.60**	**0.85**	**5.40**	**5.05**	**1.6**	**0.42**	**0.67**	-
Free Chlorine (mg/l Cl_2)	**0.07**	**0.07**	**0.07**	< 0.05	< 0.05	**1.42**	**1.31**	**0.15**	**0.06**	< 0.05	***0.05***
Ammonium (mg/l NH^4)	< 0.05	< 0.05	< 0.05	<0.05	<0.05	< 0.05	< 0.05	<0.05	< 0.05	<0.05	***2***
Nitrates (mg/l NO^{3-})	10.8	10.4	10.3	10.1	10.5	8.9	8.3	9.5	6.8	9.1	***0.3***
Nitrites (mg/l NO^{2-})	0.02	0.02	0.04	0.04	0.04	< 0.02	< 0.02	< 0.02	< 0.02	0.03	***50***
Total Aluminium (mg/l Al)	**0.018**	**0.015**	**0.011**	< 0.010	< 0.010	**0.016**	**0.021**	< 0.010	**0.034**	**0.021**	***5*** [18]
Total Arsenic (mg/l As)	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	***1***
Total Chrome (mg/l Cr)	< 0.010	< 0.010	< 0.010	< 0.010	< 0.010	< 0.010	< 0.010	< 0.010	< 0.010	< 0.010	-
Total Iron (mg/l Fe)	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	***2***
Total Cadmium (mg/l)	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	<0.001	< 0.001	< 0.001	***0.1***
Total Copper (mg/l)	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	***0.5***
Total Zinc (mg/l)	**0.43**	**0.46**	**0.42**	**0.42**	**0.47**	**0.64**	**0.62**	**0.40**	**0.26**	**0.36**	***2***
Total Cobalt (mg/l)	< 0.010	< 0.010	< 0.010	< 0.010	< 0.010	< 0.010	< 0.010	< 0.010	< 0.010	< 0.010	-
Total Nickel (mg/l)	< 0.010	< 0.010	< 0.010	< 0.010	< 0.010	< 0.010	< 0.010	< 0.010	< 0.010	< 0.010	***0.5***
Total Lead (mg/l)	< 0.010	< 0.010	< 0.010	< 0.010	< 0.010	< 0.010	< 0.010	< 0.010	< 0.010	< 0.010	***0.5***
Total Tin (mg/l)	< 0.010	< 0.010	< 0.010	< 0.010	< 0.010	< 0.010	< 0.010	< 0.010	< 0.010	< 0.010	-

[18] The French regulation considers a limit for Aluminium and Iron together. This way, the concentration of both of these pollutants in reject water must not exceed 5 mg/l of Fe + Al.

The following table presents the result that were obtain selecting only the most critical parameters and grouping them per measuring point. The most demanding value from the consulted legislations has also been included.

Table 48 – Result obtained on the most critical parameters grouped per measuring point

Point of Measure	Campaign	Samples	Parameters							
			Suspended matter (mg/l)	**DOC** (mg/l C)	**COD** (mgl/ O_2)	**AOX** (mg/l Cl^-)	**Bromine** (mg/l Br_2)	**Free Chlorine** (mg/l Cl_2)	**Total Aluminium** (mg/l Al)	**Total Zinc** (mg/l)
SF1	**1º**	**nº1** (14h12 to 19h12)	**2.2**	**14**	**56**	**0.17**	**1.19**	**0.07**	0.018	**0.43**
		nº2 (19h12 to 00h12)	< 2.0	**8.6**	33	**0.11**	**1.14**	**0.07**	0.015	**0.46**
	2º	**nº1** (14h30 to 20h30)	< 2.0	**10**	**46**	**0.10**	0.24	**0.07**	0.011	**0.42**
		nº2 (20h30 to 02h30)	< 2.0	**8.0**	24	**0.11**	0.60	< 0.05	< 0.010	**0.42**
		nº3 (15h30)	< 2.0	**7.8**	33	**0.10**	0.85	< 0.05	< 0.010	**0.47**
	3º	**nº1** (17h00)	-	**11.55**	23	< 0.01 [19]	-	< 0,05	-	< 0.1
	4º	**nº1 - CERN** (07h30)	-	**8.41**	15	***0.2*** [19]	-	**0.16**	-	**0.2**
		nº2 - CERN (10h00)	-	**8.67**	20	***0.5*** [19]	-	**0.41**	-	**0.3**
		nº3 - CERN (11h40)	-	**8.67**	15	***0.5*** [19]	-	**0.44**	-	**0.2**
		nº1 - CARSO (07h30)	-	-	-	**0.17**	-	-	-	-
		nº2 - CARSO (11h40)	-	-	-	**0.19**	-	-	-	-
Building 863	**1º**	**nº1** (16h15)	< 2.0	**9.5**	25	**0.24**	**5.40**	**1.42**	0.016	**0.64**
		nº2 (18h15)	< 2.0	7.1	24	**0.19**	**5.05**	**1.31**	0.021	**0.62**
	2º	**nº1** (15h45)	**10**	6.7	< 20.0	**0.12**	**1.6**	**0.15**	< 0.010	**0.40**
	3º	**nº1** (17h10)	-	**8.8**	16	< 0.01 [19]	-	**0.3**	-	**0.2**
Ramses	**1º**	**nº1** (16h20)	< 2.0	3.4	< 20.0	< 0.05	0.42	**0.06**	0.034	**0.26**
	2º	**nº1** (16h00)	**2.8**	6.8	**41**	**0.05**	0.67	< 0.05	0.021	**0.36**
Most Demanding Regulation Limit			***20***	***10***	***40***	***0.1***	Non Existent	***0.05***	***5 (Combined with Fe)***	***2***
Country of the Regulation			CH	CH	D	CH	Non Existent	CH	Fr	CH, FR

CH – Switzerland; D – Germany; Fr – France; Pt – Portugal;

[19] Value obtained should be disregarded due to problems with method during analyses

11 DISCUSSION OF RESULTS

11.1 Overall Analysis of the Results

The most immediate and most important result obtained from these sampling campaigns is the fact that, at the outlet (RAMSES), CERN's effluent is fully compliant with the regulation for France and Switzerland for all parameters. In fact, this situation is still verified even applying the most demanding regulation found.

This way, considering that the samples at RAMSES were representative once they comprised both regular and shock treatments (with or without de-concentration water), it can be said that the water that CERN discharges follows the regulation.

However, at the source of the effluent, Building 863 and SF1, the situation is not the same. CERN's effluent water presents non-compliances and higher values for most parameters at the source (both Building 863 and SF1).

These differences in results occur probably because, at RAMSES, the water is mixed. At point 1 of RAMSES, the water from Building 863 and SF1 is mixed not only with all the cooling water from the LHC loop but also with other water from the LHC and SPS, like the raw water overflow, infiltration and meteoric water that are basically clean water and still have considerable volumes. This way, the discharge water from the cooling circuits is, in a certain way, diluted with other waters which raise its quality at the outlet.

Although the current situation of the discharges is good, the previously presented situation brings up a possible problem. If by any reason (such as a technical change in the system) the LHC loop stops providing big volumes of clean water, the dilution of the discharges of buildings 863 and SF1 will not occur and the reject will probably be not be compliant with the regulation.

Note: Non compliances were considered to be the values that were above or approaching the limits set by the previously consulted regulations, considering not only the host states but the most demanding international regulation found.

11.2 Parameters analysis

As a result of the sampling campaigns that were carried out, the following list of problematic parameters was found:

- AOX (Adsorbable Organic Halides);
- Bromine;
- COD (Chemical Oxygen Demand);
- DOC (Dissolved Organic Carbon);
- Free Chlorine;
- Suspended matter;
- Total Aluminium;
- Total Zinc.

These parameters will be further described by reverse order of compliancy.

11.2.1 AOX

The parameter that presented the worst results was the AOX.

For Building 863 and SF1, this parameter is always non compliant with the Swiss regulation and always compliant with the French regulation. Although the question of the purpose or credibility of the low value of 0.1 mg/l of AOX set by the Swiss regulation is raised by the results obtained and by comparison with other regulation, this value must still be followed once it is the ruling legislation.

Due to a problem with the method that occurred during analyses, the values for AOX obtained in the third and fourth campaign by the CERN's environmental laboratory should be disregarded. This way, all the values obtain for AOX are relatively similar and steady above the Swiss regulation for both SF1 and building 863. Still, both in first campaign and at building 863, these values are slightly higher in average.

The highest value was found in the first campaign at Building 863. This value was 0.24 mg/l of Cl^- and it is 2,4 times higher than the Swiss legislation but 4 times inferior to the value permitted by the French law.

11.2.2 Free Chlorine and Bromine

At the time when the sampling campaigns were performed, the values of both of free chlorine and bromine are always higher at Building 863 than at SF1. They were also higher for the first sampling campaign.

The regulation of France leaves out these two pollutants while the regulation of Switzerland leaves out the bromine and considers a rather strict limit of 0.05 mg / l of Cl_2 for chlorine. Once the detection limit of the method is also 0.05 mg / l of Cl_2 whenever a result would be obtained it was already above the Swiss limits. This happened in 11 out of the 15 measurements of free chlorine done.

The values of chlorine and bromine are higher at Building 863, maybe as a result that more regular biocide per volume of water in circuit is inserted. As previously stated, building 863 holds a total volume of water of 4000 m^3 while SF1 holds a smaller total volume of 1500 m^3. As for the quantity of regular biocide, 1700 kg were applied in building 863 SF1 against 410 kg in SF1. This way, in the year 2007, the total quantities of inserted regular biocide per total volume of circuit were 0.273 kg for SF1 and 0.425 kg for building 863.

As the two main sources of chlorine and bromine in the water of the cooling circuits are the biocide products (both the regular and the shock one), and once that the shock biocide product is inserted in the same ratio for both SF1 and building 863 the different should lay in the input of the regular biocide.

The highest values of bromine were 5.4 and 5.05 mg/l of Br_2 and the highest values of Chlorine were 1.42 and 1.31 mg/l of Cl_2.

11.2.3 Chemical Oxygen Demand

Considering the parameter chemical oxygen demand and taking into account the value set by the German regulation (40 mg/l O_2), there are three situations were the limit is exceeded and many were the limit is close to being surpassed. Two of these non compliances occur at SF1 (56 and 46) and one occurs at RAMSES (41). The values for chemical oxygen demand are generally higher for SF1 than for building 863.

11.2.4 Dissolved Organic Carbon

As for the parameter dissolved organic carbon, there are 3 non compliances of the Swiss legislation value (10 mg/l of C) all of them occurring at SF1. These non compliances are distributed over the first three campaigns and take the values of 14, 10 and 11.55 mg/l of C. Both for SF1 and building 863, when these values don't exceed the limit, they are very close to exceeding the mentioned limit.

11.2.5 Suspended Matter

As for the parameter of suspended matter, although it never reached the emission limits, there are three values that raise some concern. The first of these values (2.2 mg/l) appears at SF1 on the first sample of the first campaign and it doesn't show at RAMSES. The second value (10 mg/l) appears at Building 863 on the first sample of the second campaign and it shows at RAMSES although it is reduced to 2.8 mg/l. These results evidenced that, as expected, building 863 has a bigger significance in the overall quality of CERN effluent most likely due to is large total circuit volume which also implies larger discharges.

The highest value obtained for this parameter was 10 mg/l and it is half of the limit value of 20 mg/l set by Swiss law.

11.2.6 Zinc and Aluminium

Metals are in general bioacumulable and quite toxic for most living organisms.

From the set of analyses realized, there are only two metals that present noticeable results within the set of parameters chosen. These metals were Zinc and Aluminium.

The two highest values for Zinc were found at building 863 (0.64 and 0.62 mg/l) and are three times inferior to the Swiss and French legislation limit of 2 mg/l of Zn.

It is likely that the Zinc found in the analyses is originating in the anti-scaling and anti-corrosion product used in regular treatment once this product contains Zinc Chloride.

The values obtained for this parameter were always higher at building 863 than at SF1 and they seem to vary little within the results analyses performed by CARSO.

It was expected that the values of zinc would not change according to the presence of shock treatment products once these products do not contain zinc.

However, it was not expected that the concentration of zinc was higher at building 863 than at SF1, once that slightly more anti scaling and anti corrosion product per volume of circuit is inserted at SF1. The inserted quantities of this product, in the year of 2007, per total volume of circuit were 0.91 l for SF1 and 0.835 l for building 863.

The Aluminium values were also noticeable but still quite below the French regulation that sets a value of 5 mg/l of Al + Fe. This was the most demanding value found for this parameter.

Contrary to the rest of the pollutants, the values obtained for Aluminium were higher at RAMSES than at building 863 and SF1 which indicates that most likely this pollutant originates at other point of CERN's site drainage.

11.2.7 Analysing the relations between parameters

As demonstrated by all the figures presented in this chapter, when analysing over time, while time passes away from the moment of the injection of the products in the circuits, the parameters of suspended matter, DOC and COD seem to drop. The concentration of AOX and free chlorine seems to stay relatively stable along the time interval of these measurements but the concentration of bromine rises significantly in the second campaign at SF1.

Note: The Y row values always represent the concentration of pollutant in mg/l, in all figures with the exception of figure XXV.

Note: the notation 1ºC means first campaign

The following two graphics show the relation between some of the parameters that were analyzed at CARSO laboratory in all the sampling campaign where samples were sent to CARSO.

The first figure shows the behaviour of the following parameters: Suspended Matter, DOC, BOD_5, AOX, Bromine, Free Chlorine, Ammonium, Nitrates in the different campaigns.

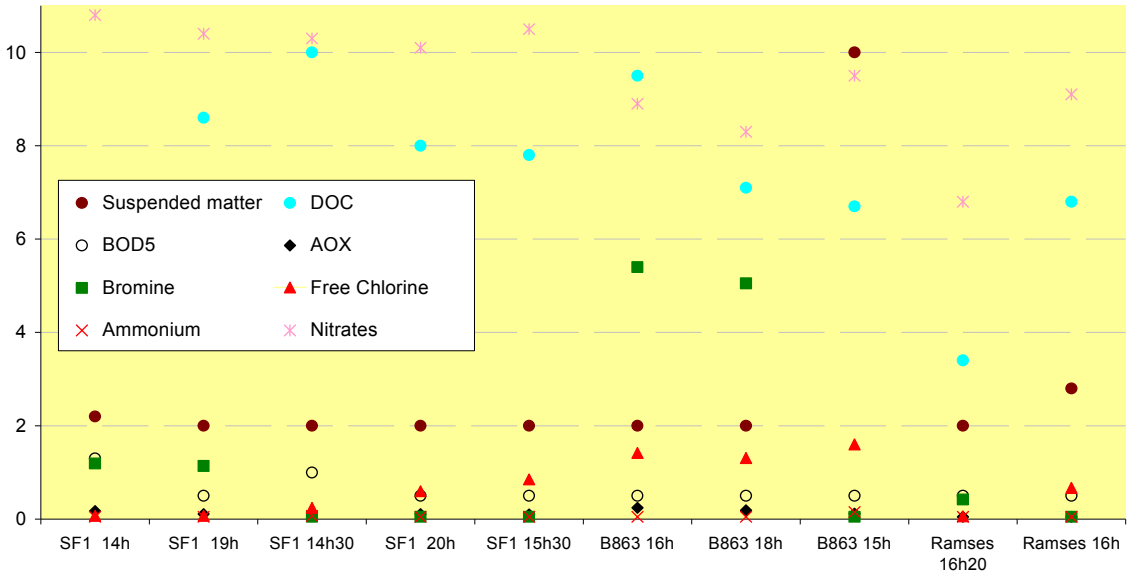


Figure XX – Graphic with the problematic parameter values obtained in the different campaigns by CARSO

For both of the parameters Zinc and Aluminium, there seems to be no relation either between them or with any of the other pollutants.

It is possible that there is a relation between the concentration levels of AOX and any other parameters included into figure XIX, especially when considering the parameter dissolved organic oxygen. It seems also that there is a direct relation between the values of AOX and the values both of free chlorine and of free bromine.

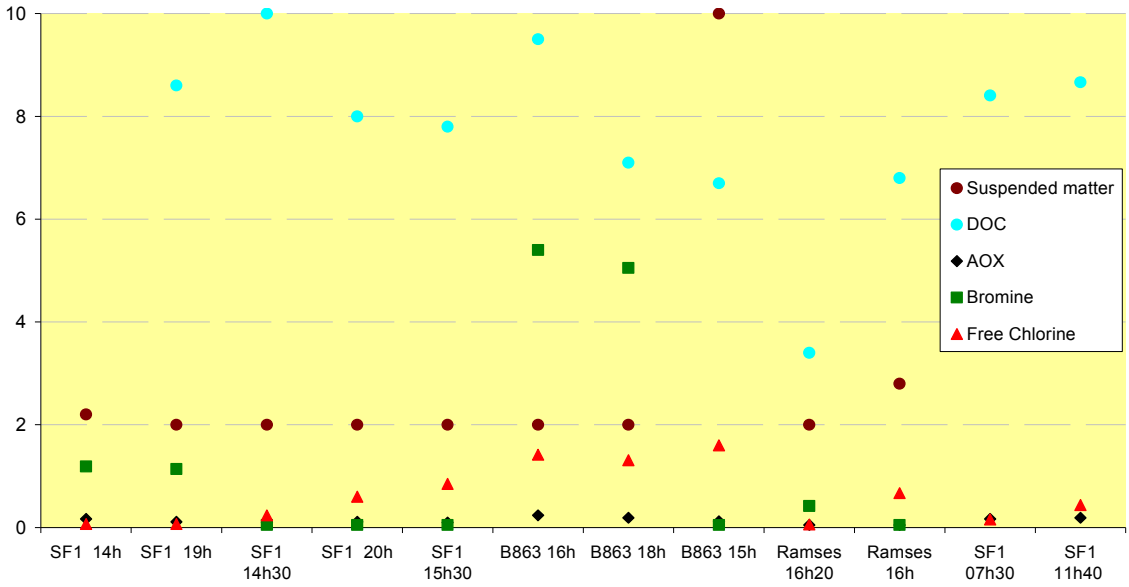


Figure XXI – Relation between suspended matter, DOC, AOX, Free Chlorine and Bromine

Concerning the most demanding regulation, which in case of free chlorine and AOX is the Swiss regulation, limit values are constantly exceeded in building 863 and SF1. In fact, limits are only respected when the values are below measuring range.

Bromine has no limit values. However, if limits would be similar to free chlorine limits the compliance situation for the parameter bromine would be similar. Figure XX, illustrates well this scenery.

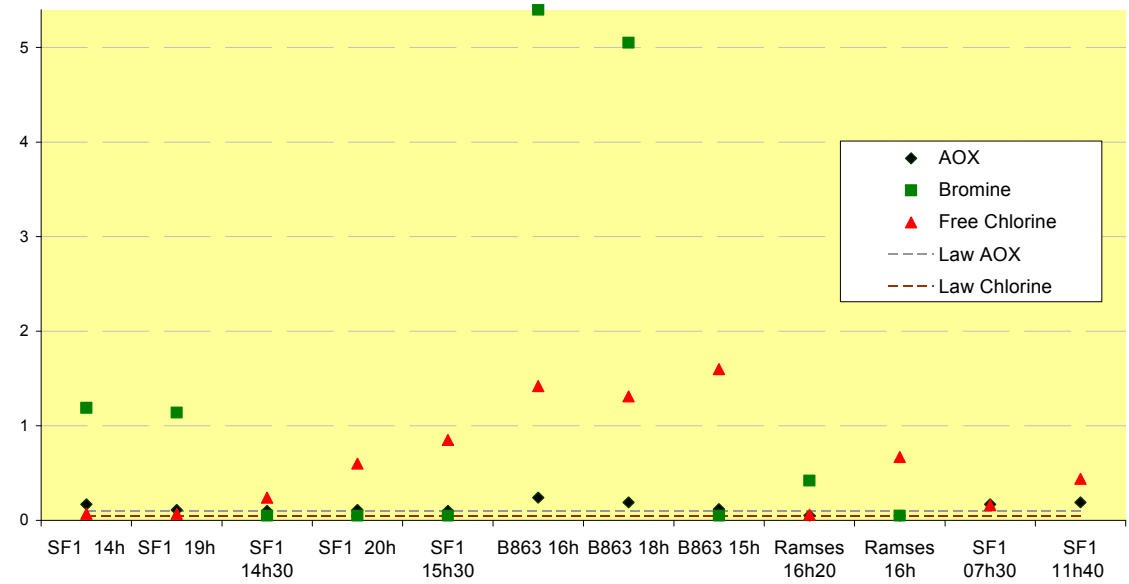


Figure XXII – Relation between AOX, Bromine and free Chlorine in the obtained results

The concentrations of the pollutants Zinc and Aluminium doesn't seem to be affected by the choice of time of the sampling as shown in the figure XXI.

The same Figure, also shows that the limits set by the consulted regulations both Aluminium and Zinc are well within control.

It remains important to notice that in first campaign only two samples were done at SF1 whereas in second campaign 3 samples were made.

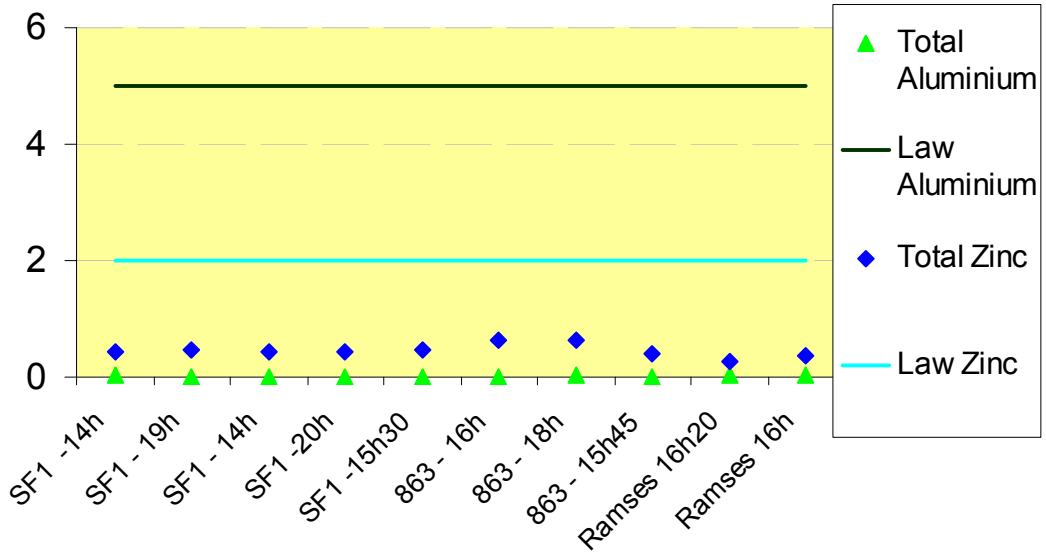


Figure XXIII – Zinc and Aluminium concentration over time

Next figure establishes an important point by comparing several parameters values obtained in the two sampling campaigns at RAMSES. The analysis of the graphic values shows that the values of the second campaign are generally higher.

Having in mind that only the sample taken on the second campaign contains the discharge of de-concentration water from SF1 and building 863 and that the overall

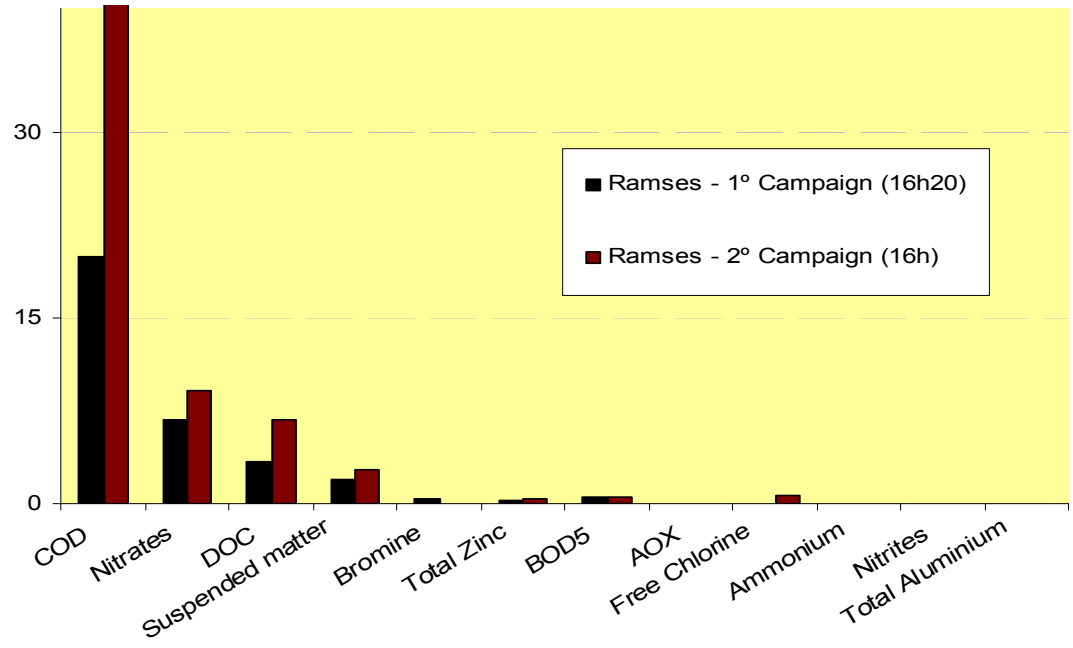


Figure XXIV – Comparison between both samples at RAMSES

values of the first campaign are higher, we can have a measure of the influence of the de-concentration water from SF1 and building 863 in the overall quality of the effluent that passes at RAMES. Furthermore, de-concentration water is the biggest and probably most representative discharge from the cooling circuits

The following two figures, numbered XXIII and XXIV, shows the results from 1º, 2º and 3º campaign divided by point of sampling.

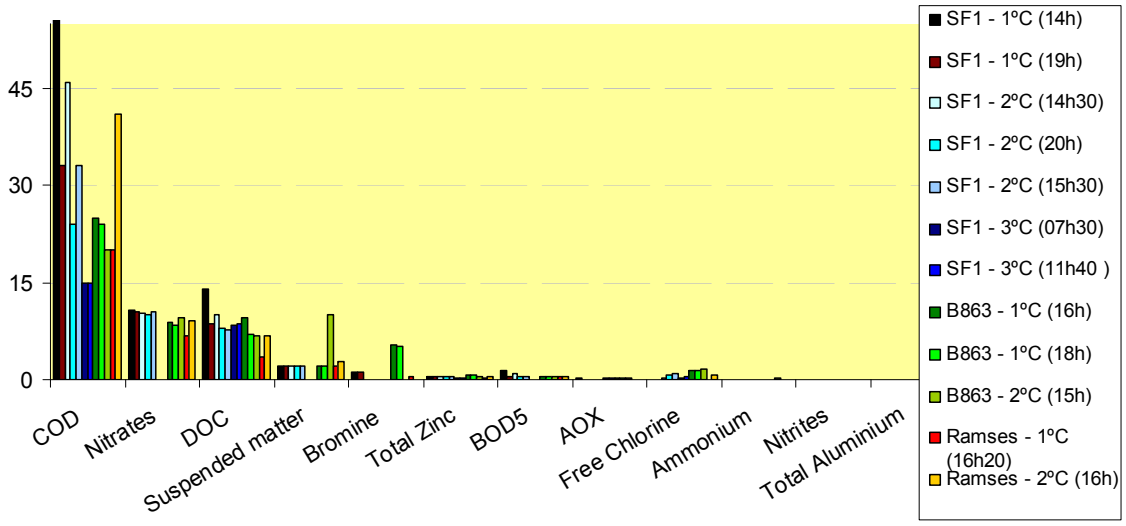


Figure XXV - Results from 1º, 2º and 3º campaign divided by point of sampling (part I)

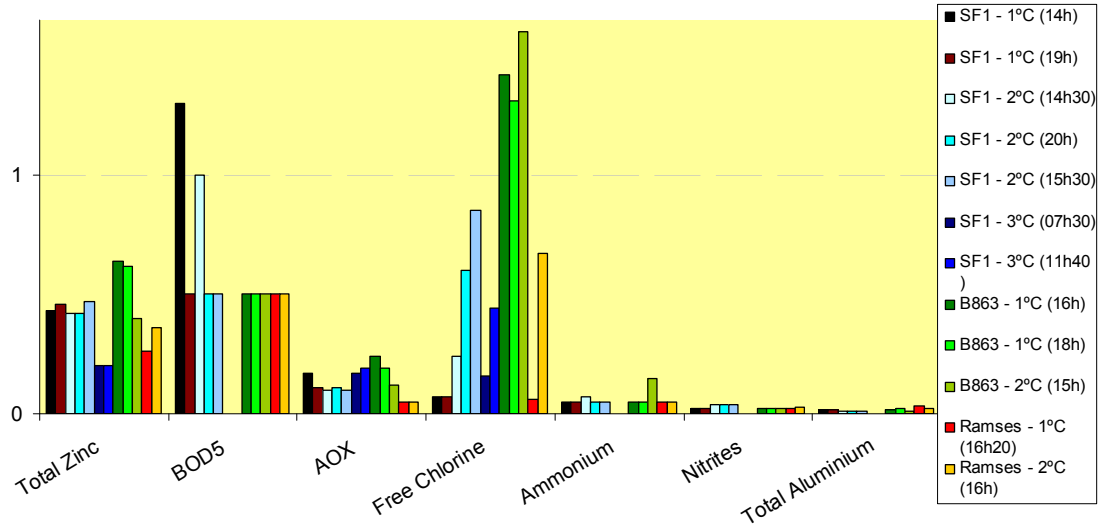


Figure XXVI - Results from 1º, 2º and 3º campaign divided by point of sampling (part II)

This graph shows the main parameters over all the campaigns were CARSO laboratory made analyses.
A logarithmical scale was used to make possible the comparison between parameters with different value ranges, this only the relative differences are important in this graphic.

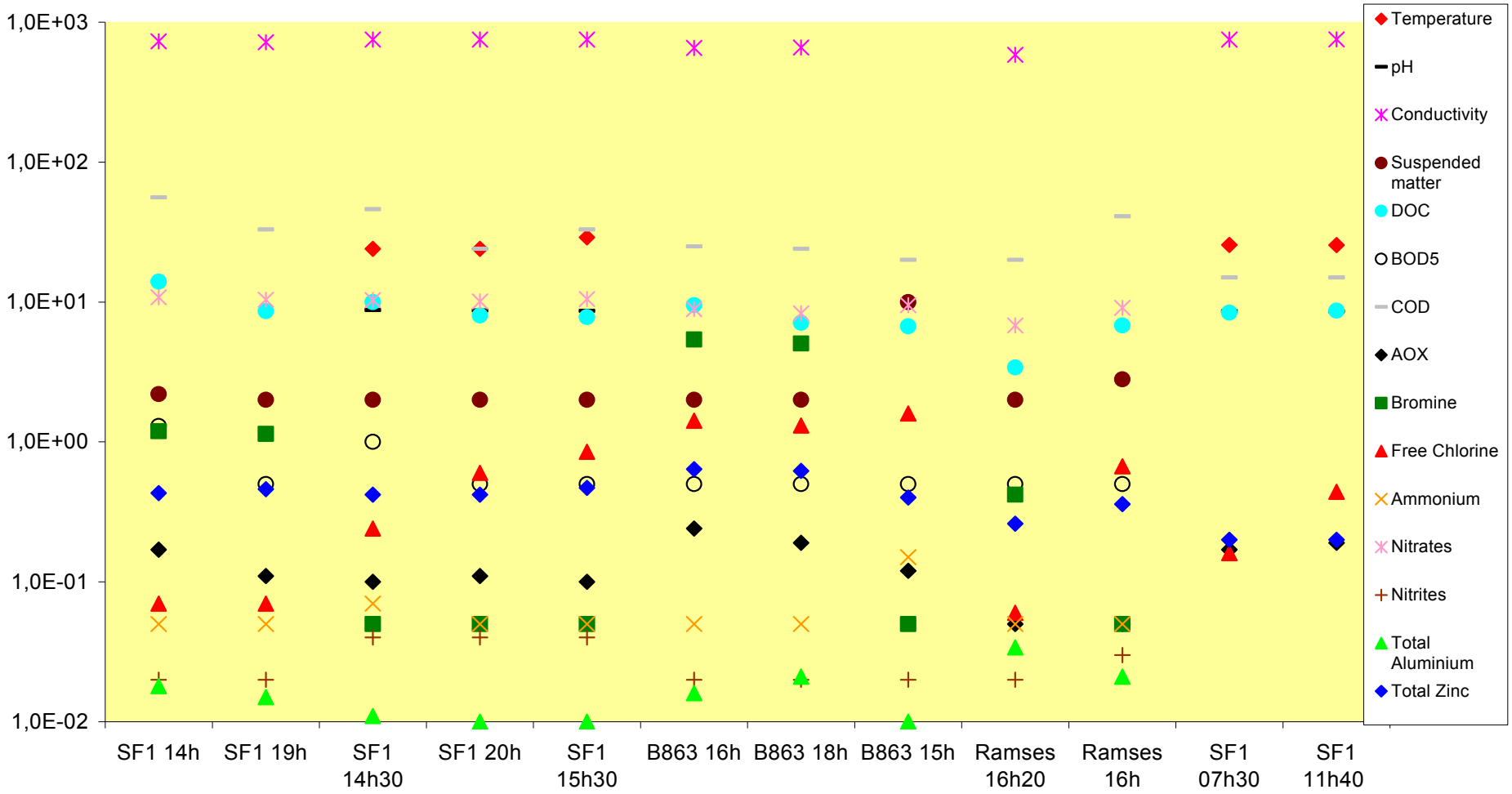


Figure XXVII – Main parameters analysed at CARSO in a logarithmical scale.

12 PROPOSALS FOR THE FUTURE

The last part of this work attempted to present possible routes for future improvements.

12.1 Toxicity tests – A viable way to assess the overall quality of an effluent?

After analyzing CERN's cooling water using conventional water quality parameters, this work embraced a search for alternatives ways of conducting water testing because the values provided by conventional tests are often expensive to obtain and do not present a clear picture of the overall toxicity of an effluent, disregarding, for example, the synergetic effects of two or more pollutants and their interactions in the environment.

Toxicity observed in effluents can be caused by a large number of factors that can act independently or jointly. According to Society of Environmental Toxicology and Chemistry (SETAC), a general description of these factors includes the following:

- Chemical Factors
  - Inorganic chemicals (e.g., ammonia, chlorine, and heavy metals);
  - Organic chemicals (e.g., dioxins, polychlorinated biphenyls and surfactants);
  - Pesticides (e.g., chlorpyrifos, diazinon, and heptachlor).

- Physical Factors
  - Dissolved and suspended solids;
  - Temperature.

- Biological Factors
  - Bacteria;
  - Fungi;
  - Parasitic invertebrates.

Toxicity observed in effluents has been attributed to several chemicals commonly found in or added to wastewaters, including chlorine used for disinfection and ammonia related by the breakdown of organic substances in domestic wastewater.

Cooling water systems, such as CERN's, use biocides that are intentionally added to control nuisance biological growth. When discharged, these chemicals can retain their toxic characteristics and may be harmful to aquatic life in receiving streams.

Domestic wastewater systems receive many household chemicals that are improperly disposed of, including organic solvents and pesticides. Some commonly used soaps and detergents, particularly some commercial detergents, have proven highly toxic if inadequately treated prior to discharge.

Recently, it has also been established that a number of elements and compounds commonly found in aquatic ecosystems can be toxic to aquatic organisms when present

in concentrations above or below an organism's physiological tolerance level. Ions such as potassium, magnesium, and calcium, all of which are essential elements used by organisms, can be toxic when the ions are added or taken out of water during various industrial processes.

As it was understood in the present study, also aquatic toxicologists realized a number of years ago that it was not possible to test all chemicals and possible combinations of chemicals that may occur in certain effluents. This reality coupled with the fact that there were few toxicity data for the vast majority of chemicals in commerce, led to the appearance of ecotoxicological tests in effluents and streams influenced by industrial and wastewater treatment facilities. These toxicity analyses were conducted in combination with chemical analyses to better link the measurements of toxicity with specific chemicals that produce it.

As toxicity tests were refined, more formalized laboratory tests were developed that included multiple dilutions and treatments. This way, methods and species became standardized, allowing for comparison among tests and aqueous samples.
Biomonitoring approaches (sampling and identification of aquatic populations living in a body of water) were added to chemical-specific and toxicity tests regulations to provide additional information on water quality in aquatic ecosystems.

These tests are becoming widely applied to ambient stream samples to detect not only point source effects but also the cumulative effects of non-point sources of pollution like urban or agricultural runoff.

Some regulatory approaches focus on controlling toxic amounts of individual chemicals known to be present in the effluent. In contrast, ecotoxicological test actually measures the potential toxicity of all chemicals in a solution. Furthermore, this type of testing may even show that chemicals known to be toxic to aquatic organisms may be rendered non-toxic or less toxic by particular characteristics of the effluent matrix and/or receiving stream chemistry.

12.1.1 Fifth Sampling Campaign

This way, 4 different types of ecotoxicological tests were studied and applied:

- Green Algae Test;
- Luminiscent Bacteria Test (Microtox);
- Micro-crustaceans Test (Daphnia Magna);
- Macrophytes (Lemma Minor).

In order to apply these tests, CERN contacted a Swiss company named Soluval, specialized in ecotoxicological tests.

The following table contains a brief description of the main characteristics of the bioassays that were used. It also provides information about the norms used:

Table 49 – Fifth Campaign: Ecotoxicity test, Duration of test, Measured effect and Norms used

Ecotoxicity Test	Green Algae	Luminescent Bacteria (Microtox)	Micro-crustaceans	Macrophytes
Specie	Pseudokircheneriella subcapitata	Vibrio Fischeri	Daphnia Magna	Lemma minor
Duration of test	72 hours	5, 15 and 30 minutes	24h and 48h	7 days
Measured effect	Inhibition of bioluminescence	Growth inhibition	Survival rate	Growth inhibition
Type of Toxicity	Chronic	Acute	Acute	Chronic
Norm	ISO 8692 / OECD 201	ISO 11348-3 / AFNOR T 90-320	ISO 8692 / OCDE 202	ISO/CD 20079 AFNOR T 90-337
Blank controls results with toxic reference substances are compliant with guidelines, thus validating the result obtained.				

The samples analysed by Soluval were taken on the fifth and final sampling campaign of this study.
These samples were analysed at Soluval on 12 of December of 2007.

The procedures were similar to the previous campaigns. Samples were, once more, collected in a punctual way from SF1, building 863 and RAMSES.

The following table describes the location, type of sample taken and the nature of the samples:

Table 50 - Location, type of sample taken and the contents of the samples of fifth sample

Fifth Sampling Campaign (Ecotoxicity tests)		
Point of Measure	**SF1**	**RAMSES**
Number of samples taken	1	1
Type of sampling	Punctual	Punctual
Location	Manhole outside SF1	Manhole outside PA1
Nature of sample	De-concentration water from SF1	Global effluents from the site collected (including the de-concentration from SF1 and building 863)
Type of treatment	Regular Treatment	Regular Treatment
Analyser	Soluval	Soluval

As done in the previous campaigns, samples were kept in the refrigerator overnight and sent inside a cooler box containing cooler elements to preserve the samples characteristics.

In this campaign, the delivery of the sample was done by post and not in person. However, it was insured that the delivery would not take more than 8 hours.

The bioassays conducted at Soluval on SF1's sample have been conducted after adjusting the pH solution to a pH appropriate to organisms, according to the standards. This way the initial pH of 8,8 was adjusted to 8.

The pH of the sample of RAMSES was not adjusted.

The conductivity of sample of RAMSES was K = 325 µS/cm while for sample of SF1 it was K = 695 µS/cm)

The algal assay was performed on solutions with added nutrients, in order to insure that there would not be lack of nutrients for the algae in the sample. According to the ISO 8692, the nutrient medium contained macronutrients (N, P, K, M, Ca), as well as traces of elements (Fe, B, Mn), the chelating agent EDTA and sodium carbonate, at final concentrations equalling those in the controls.

12.1.2 Research on the toxicity classification

Knowing that performing eco-toxicity tests would provide values on the quality of an effluent, a vital step was to better understand the meaning of the values provided by these tests. Research showed that the results for toxicity tests can be interpreted in different ways according to different scales.[20]

The following two types of values were found to be the most used in ecotoxicity tests and are bellow analysed and described:

Table 51 – Description of ecotoxicity parameters

Parameter	Description
EC	Effective Concentration of a sample that cause 20% (EC_{20}) or 50% (EC_{50}) inhibition in the luminescent bacteria test;
GL	Dilution Level at which a sample causes less than 20% inhibition;

The following two articles set classifications for toxicity of EC and GL values:

In the article "*Toxicity evaluation of Reactive dyestuffs, auxiliaries and selected effluents in textile finishing industry to luminescent bacteria Vibrio fischeri*" from Wang C. et al.

Table 52 – Toxicity classification using the GL parameter according to Wang et al.

Toxicity Classification	Parameter	Range of parameters values for sample
Low	GL	< 10
Moderate	GL	≥ 10 and < 100
High	GL	≥ 100

In the article "*Aquatic toxicity emission from Tokyo: wastewater measured using marine luminescent bacterium, photobacterium phosphoreum*" from Asami M. et al

Table 53 - Toxicity classification using the EC parameter according to Asami et al.

Toxicity Classification	Parameter	Range of parameters values for sample
Non Toxic or slightly toxic	EC_{50}	> 1
Low toxicity	EC_{50}	≤ 1 and > 0.2
High toxicity	EC_{50}	≤ 0.2

[20] Additionally, annex 8 show a method for evaluation of the ecotoxological risk

However, both articles mentioned were unclear to why they set these values for toxicity, supplying no information on the origin of the given classification.

In addition, as previously stated in chapter 9, the German law contemplates the use ecotoxicity tests, through the GL value, as a way to measure toxicity of effluents, in general, and cooling systems effluents subject to treatment with biocide, in particular. German Law establishes a GL value of 12 as a limit for effluent.
For Chemical industry, the same regulation sets a value of 32.

12.1.3 Soluval's toxicity classification

Soluval company uses the following ecotoxicity classification that is within the frame of the methodological working group "Tests Écotoxicologiques" of the CIPEL commission (Comm. internationale pour la protection des eaux du Léman contre la pollution, Lausanne).
This classification has been proposed to describe the ecotoxicological quality of wastewaters and effluents from sewage treatment plants. This ranking allows to qualify the ecotoxicity of samples, simplifying the comparison from site to site and the transmission of results. The table bellow shows this classification:

Table 54 – Ecotoxicity classes considered by Soluval

Ecotoxicity class	***I.* Non toxic**	***II.* Slightly toxic**	***III.* Toxic**	***IV.* Highly toxic**
Toxicity Test Result	EC_{50} not measurable (or $EC_{20} > 50$ %)	$EC_{50} > 50$ %	$EC_{50} < 50$ %	$EC_{50} < 10$ %
	$TU_{50} < 1{,}0$	$TU_{50} < 2{,}0$	$TU_{50} > 2{,}0$	$TU_{50} > 10$
The class of a sample is defined by the most sensitive effect concentration from various tests and exposure times				

Bioassay results were integrated and expressed by the estimated concentration of the sample that induces an inhibition of 50% or X% of the organism activity with respect to the control (EC_{50} or ECX) at the end of the test.

The lower is the EC50 or ECX value, more toxic is the solution.
The values of EC were reported with 95% confidence limits.

Results can also be converted to *Toxic Units (TU)* according to the following formula:

$$\textit{Toxic Units } (TU_{50}) = 100 / EC_{50}.$$

The value of toxic units for a sample corresponds to the dilution factor necessary to induce an inhibitory effect of 50% on the organism's activity in the assay conditions. Usually, a sample is considered as toxic when the EC_{50} value is 100% (undiluted wastewater) or lower, thus when *Toxic Units* are above 1.

12.1.4 Analyses of the results of the fifth campaign

The following two tables synthesize the results obtained from the ecotoxicological tests:

Table 55 – Ecotoxicity results for Sample A – RAMSES [21]

Samples A - RAMSES (on 12-12-2007, pH = 8.1, K = 325)						
Ecotoxicity Test		**Green Algae**	**Luminescent Bacteria (Microtox)**	**Micro-crustaceans**		**Macrophytes**
Specie		Pseudokircheneriella subcapitata	Vibrio Fischeri	Daphnia Magna		Lemma minor
Duration of test		72 hours	5, 15 and 30 minutes	24h	48h	7 days
Classification		Not toxic (Stimulation)	Not toxic	Not toxic	Not toxic	Not toxic
Effective Concentration	EC_{20}					
	EC_{50}					
Toxic Units (TU)		≤ 0.5	≤ 0.5	≤ 0.5	≤ 0.5	≤ 0.5
The class of a sample is defined by the most sensitive effect concentration from various tests and exposure times						

Table 56 - Ecotoxicity results for Sample B – SF1 [20]

Samples B - SF1 (on 12-12-2007, pH adjusted to 8.1, K = 325)						
Ecotoxicity Test		**Green Algae**	**Luminescent Bacteria (Microtox)**	**Micro-crustaceans**		**Macrophytes**
Specie		Pseudokircheneriella subcapitata	Vibrio Fischeri	Daphnia Magna		Lemma minor
Duration of test		72 hours	5, 15 and 30 minutes	24h	48h	7 days
Classification		Toxic	Slightly Toxic	Slighty toxic	Toxic	Slightly Toxic
Effective Concentration	EC_{20}	-	50.1% [40.8– 61.6%]	-	-	72.3%
	EC_{50}	14.2% [13.5 – 19.5 %]	-	-	58.8% [54.3– 62.9%]	-
Toxic Units (TU)		7.1	≤ 0.7	≤ 0.5	1.7	≤ 0.5
The class of a sample is defined by the most sensitive effect concentration from various tests and exposure times						

[21] Further details about results are given in annex

Sample A. – Ramses

Bioassay results with different organisms do not show any significant effect, neither of acute toxicity (daphnids and luminescent bacteria) nor of chronic toxicity on green algae. Even when prolonging the test duration with daphnids to 72 hours, no inhibition of their mobility is observed. As for the tests with green algae, a relative stimulation in their growth could even be noticed.

Sample B. – SF1

Results for daphnids and green algae bioassays indicate an obvious toxicity whereas luminescent bacteria or Lemma minor appear to be less sensitive to the sample.

Although, the inhibition of daphnids mobility is reduced within the first 24 hours, it becomes quite noticeable when prolonging the test for 48 hours of exposure providing the values of $EC_{50\,(48h)}$ = 58,8 % and TU_{50} = 1,7.
The bioassay with green algae shows a significant growth inhibition. The values of $EC_{50\,(72h)}$ = 14,2 % and TU_{50} = 7,1 were the highest obtained.

Therefore the sample taken at SF1 is considered as toxic.

In conclusion, based upon the obtained data, the ecotoxicological quality of the taken at RAMSES is considered as non toxic (class I of the above mentioned classification), whereas that of the sample taken at SF1 is considered as toxic (class III).

It is important to point out that the sample A, taken at RAMSES, does not induce any toxic effect on the tested organisms, whereas sample B, taken at SF1, induces a significant toxicity on the daphnids and on the green algae.

12.1.5 WET – Whole Effluent Toxicity

Still concerning ecotoxicity, one extra system of tests was found in literature and used as comparison.

Whole Effluent Toxicity (WET) is a term used to describe the aggregate toxic effect of an aqueous sample as measured by an organism's response upon exposure to the sample. The aqueous sample can be, for example, a whole effluent wastewater discharge and the most commonly measured responses are lethality, impaired growth or reproduction.

WET tests are aimed at replicating, to the greatest extent possible, the total effect and actual environmental exposure of aquatic life to toxic pollutants in an effluent without requiring the identification of the specific pollutants.

Whole Effluent Toxicity testing is being used by United States Environmental Protection Agency's (EPA) as an important component of the integrated approach for detecting and addressing toxicity in surface waters.

The Clean Water Act controls water pollution in the United States by regulating effluent discharges into water courses. WET tests are included within the National Pollutant Discharge Elimination System (NPDES) permit program that is authorized by the Clean Water Act. These permits specify the conditions that must be met prior to discharging and often include WET tests as a monitoring requirement and sometimes for compliance determination.

EPA's promulgated WET test methods include two basic types of WET tests:

- Acute test;
- Chronic test.

Acute tests have a duration of 96 hours or less and the endpoint is generally mortality. Chronic test have a duration of 7 day life cycle or more and the endpoints can be growth, reproduction, and mortality.

EPA has developed WET test protocols using both freshwater and marine and estuarine test species. EPA recommends running tests using an invertebrate, vertebrate and a plant to identify the most sensitive species.

Organisms used in WET tests (e.g., Ceriodaphnia dubia (freshwater flea) and Pimephales promelas (fathead minnow) are indicators or surrogates for the aquatic community to be protected, and a measure of the real biological impact from exposure to the toxic pollutants. To protect water quality, EPA recommends that WET tests be used in NPDES permits together with requirements based on chemical-specific water quality criteria.

WET tests are designed to predict the impact and toxicity of effluents discharges from point sources into U.S. waters. WET limits developed by permitting authorities are included in NPDES permits to ensure that state or tribal water quality criteria for toxicity are met. Toxicity criteria may be expressed as either numeric criteria or narrative criteria (e.g., no toxics in toxic amounts). WET monitoring requirements are included in NPDES permits to generate data for use in assessing whether a WET limit has been exceeded (i.e. compliance monitoring) or to assess if a WET limit is needed.

12.2 Renewable energy opportunities at CERN's water cooling systems

Although outside of the scope of this work, after the study of CERN's water cooling systems, one strong and compelling fact was evident.

The 500 MW of heat that CERN's water cooling systems are removing from the water and releasing into the environment is a significant figure, especially if seen in terms of renewable energy.

According to the press release done by PowerLight Corporation in 27 of April of 2006, the world's biggest photovoltaic solar power plant built in Serpa covers an area of 60 hectares using 52000 solar panels in an 11 megawatts project. [33]

If only 1% of the energy that is dissipated at CERN's cooling towers could be harness and transformed into electricity, it would have a similar positive impact on the environment as building a renewable power plant with half the size of the world biggest photovoltaic solar power plant.

In addition, if the conversion of that energy to electricity through a system with turbines would not be feasible from an engineering or economical point of view, the warm water (that is generally released at around temperature 25 ºC) could still be used for other purposes, such as heating or cooling of space (cooling of spaces can be done using hot water through a process of evaporative cooling).

Once this water is treated with biocides and thoroughly controlled, it should not be a problem to re-use this water, fact which would also result in a later discharge of the chemical products of the treatment to the water.

If a project with these characteristics would be viable, CERN could help to decrease CO_2 emissions favouring sustainable policies while profiting from a reduction on the water energy and water bills.

13 OVERALL CONCLUSIONS

The main conclusion of the conventional parameter analyses is that CERN's global effluent passing through RAMSES at point 1 was fully compliant with the limits of the regulation not only of the host states but also with the most demanding limits found. This conclusion is supported by the use of ecotoxicological tests, once that the results obtained show that the effluent at RAMSES is not toxic.

However, at the source of the effluents, Building 863 and SF1, the situation is not the same. Concerning conventional parameters, CERN's effluent water presents non-compliances with the consulted regulation and higher values for most parameters at the source (both Building 863 and SF1) were found. The ecotoxicological tests showed, as well, that the effluents discharged from the cooling circuits SF1 and building 863 are toxic. This fact, also comes in line with the previously obtained results for the conventional parameters.

The differences in results between RAMSES and the analysed cooling water discharge sources (SF1 and building 863), occur probably because, at RAMSES, the water is mixed. At point 1 of RAMSES, the water from Building 863 and SF1 is mixed not only with all the cooling water from the LHC loop but also with other water from the LHC and SPS, like the raw water overflow, infiltration and meteoric water that are basically clean water and still have considerable volumes. This way, the discharge water from the cooling circuits is, in a certain way, diluted with other waters which raise its quality at the outlet.

Although the current situation of the discharges is good, the previously presented situation brings up a possible problem. If by any reason (such as a technical change in the system) the LHC loop stops providing big volumes of clean water, the dilution of the discharges of buildings 863 and SF1 will not occur and the reject will probably be not be compliant with the regulation.

This work considered that the most important conventional parameters to control and their limits are as shown in the following list:

Table 57 – Recommended Emission Limits for the Discharge of CERN's cooling water

Emission Limits for Discharge of Effluents		
Parameter	**Units**	**Value**
Temperature	Celsius	**30**
pH	Sorensen Scale	**6.5 - 9**
Conductivity	µS/cm	**100 – 900**
Suspended matter	mg/l	**20**
DOC (Dissolved organic carbon)	mg/l C	**10**
COD (Chemical oxygen demand)	mg/l O_2	**40**
AOX (Adsorbable organic Halides)	mg/l X	**0.1**
Zinc	mg/l Zn	**2**
Free Chloride	mg/ l Cl_2	**0.5**
Free Brome	mg/ l Br_2	**0.5**

This work considers that CERN is on the right path to establish a coherent and successful Internal Regulation on the release of effluents containing water from cooling circuits, if so comes to be necessary in the future.

The ecotoxicological tests using green algae present the highest toxicity, showing that the Green Algae test is the most sensitive (within the tests carried out) to the pollutants in the effluents holding cooling water from Building 863 and SF1. The *Daphnia magna* test also presented a classification of "Toxic".

It seems likely that a conventional parameter check on above mentioned parameters combined with eco-toxicity tests would be an advantage, enabling CERN to have clearer picture of its effluents quality increasing.
The combination of both types of water testing would bring added reliability to the obtained results and maybe even benefits in reduction of cost and time to perform the analyses.

This study, as shown as well, that the de-concentration water is the most significant discharge from both of the studied cooling circuits (SF1 and building 863).
It also was found that the cooling water that is discharged from these two cooling circuits has an impact on the global quality of the effluents discharged by CERN into the river Nant d'Avril.

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Links

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2. Wikipedia LHC:
   http://en.wikipedia.org/wiki/Large_Hadron_Collider

3. Safety Commission Mandate:
   http://safety-commission.web.cern.ch/safety-commission/SC-site/sc_pages/sc_ie.htm

4. Wikipedia PS:
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6. CERN's public site – CERN and environment:
   http://cernenviro.web.cern.ch/CERNenviro/web/main/main.php?sctr=aspect&cat=4&lang=en&doc=1

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16. US Department of Labor (Occupational Safety & Health Administration):
http://www.osha.gov/dts/osta/otm/legionnaires/sampling.html

17. MBS – Journal on Modern Building Services:
http://www.modbs.co.uk/news/fullstory.php/aid/887/Restoring_the_reputation_of_the_cooling_tower.html

18. Definition of the ISO norm 9562:2004 on the AOX test:
http://webstore.ansi.org/RecordDetail.aspx?sku=ISO+9562%3A2004

19. CERN's Environmental Management System:
http://cernenviro.web.cern.ch/cernenviro/web/main/main.php?sctr=ems&lang=en&doc=1

20. CERN's public site – CERN and environmental impact:
http://environmental-impact.web.cern.ch/environmental-impact/en/EnvImpact/EnvImpact-en.html

21. CERN's public site – CERN and environment:
http://cernenviro.web.cern.ch/CERNenviro/web/main/main.php?sctr=aspect&cat=4&lang=en&doc=1

22. CERN's TS department:
https://edms.cern.ch/cedar/plsql/navigation.tree?cookie=6143264&p_top_id=1945124478&p_top_type=P&p_open_id=1114455207&p_open_type=P

23. Water pollution prevention – European Regulations:
http://www.europa.eu.int/eur-lex/en/lif/reg/en_register_15102020.html

24. Water pollution prevention – European Regulations:
http://www.europa.eu.int/eur-lex/en/lif/reg/en_register_15102050.html

25. Water pollution prevention – European Regulations:
http://www.europa.eu.int/eur-lex/en/lif/ind/en_analytical_index_15.html

26. French regulation on cooling towers:
http://aida.ineris.fr/textes/arretes/text3667.htm

27. The guidelines by EPA:
http://www.epa.gov/fedrgstr/EPA-WATER/2002/November/Day-9/w29072.htm

28. Society of Environmental Toxicology and Chemistry (SETAC):
http://www.setac.org/wetindex.html

29. U.S. National Pollutant Discharge Elimination System (NPDES):
http://cfpub.epa.gov/npdes/wqbasedpermitting/wet.cfm

30. International Commission for the Protection of Lake Geneva (CIPEL):
http://www.cipel.org/sp/secteur.php3?id_rubrique=1

31. Ambriex Company – Microtox test:
http://ambriex.net/Produto.aspx?idProduct=35

32. *Guide pour l'utilisation des tests écotoxicologiques avec les daphnies, les bactéries luminescentes et les algues vertes, appliqués aux échantillons de l'environnement* (2002). Soluval Santiago, Couvet (éd.):
http://www.cipel.org/sp/article24.html

33. According to the press release done by PowerLight Corporation in 27 of April of 2006:
http://www.renewableenergyworld.com/rea/partner/story?id=44745

34. Information on the compound 5-Chloro-2-methyl-4-isothiazoline-3-one:
http://www.toxinfo.se/english/exampl12.htm

35. Toxicity Studies for 5,5-Dimethylhydantoin:
http://www.pesticideinfo.org/List_AquireAll.jsp?Rec_Id=PC40221

36. Toxicity study on Brominated compounds:
http://www.inchem.org/documents/cicads/cicads/cicad66.htm#10.1

37. Information on the compound Bromo-5,5-Dimethylimidazolidine-2,4-dione:
http://www.chemblink.com/products/16079-88-2.htm

38. Information on Zinc Chloride:
http://en.wikipedia.org/wiki/Zinc_chloride

39. Safety data for 1,3-dichloro-5,5-dimethylhydantoin:
http://physchem.ox.ac.uk/MSDS/DI/1,3-dichloro-5,5-dimethylhydantoin.html

ANNEX

Annex 1 – Description of Nant d'Avril

Nant d'Avril is a small Genevian river whose spring is located in Mategnin (Commune de Meyrin). In Peney, Nant d'Avril merges with a river of bigger dimensions called le Rhône.

Nant d'Avril is the river that receives the biggest amount of reject water from CERN's site drainage. The water discharged into Nant d'Avril represents more than half of the total water that is discharged by CERN's site drainage network.

According to the paper "*Rapport n5 sur les measures de la radioactivite dans le nant d'avril*" from the university of Geneve, Nant d'Avril has a hydrographical basin of 16,8 km^2 that is located in the Swiss districts of Meryn, Satigny and Vernier and in the French district of l'Ain. These areas are strongly occupied by human constructions and 21% of the surface of the basin is considered as impervious to water whereas 14% is occupied by florests, 38% by cultivated land and 25% by prairies.

The same study, also divulges the average natural flow of this river which is within the range of 0,3 to 0,4 m^3/s. This river is strongly influenced by CERN's cooling water discharges that represent an average flow of 0,2 m^3/s.

The upper part of the river is channelled through a gallery constructed in concrete that runs for a distance of 2870m. This gallery goes bellow the "route de Meryn" and passing after bellow to the "route du Mandement" before it reaches its natural environment. CERN's water discharges from the site drainage network to the Nant d'Avril are done in 3 different points of the gallery that runs under the route de Meyrin.

The following image shows Nant d'Avril in a location close to CERN during the summer of 2007.

Figure XXVIII – Nant d'Avril

Annex 2 – Controversy on the value of the AOX parameter

Initial research on the parameter AOX has shown that different countries have a very different approaches and regulation.

In the host states:

- FRENCH Regulation considers the limit 1,0 mg/L of AOX;
- SWISS Regulation considers the limit 0,1 mg/L of AOX.

In the world:

- USA Regulation does not consider AOX an important parameter;
- GERMAN Regulation considers AOX an important parameter. (0.15 mg/l AOX)

According to Leo Nollet, in the "handbook of water analysis":

TOX = POX + EOX

Where:

TOX – Total Organic Halides
POX – Purgeable Organic Halide
EOX – Extractable Organic Halides

Water treatment with Chlorine leads to the formation of Trihalomethane Polychorinated Biphenis (PCBs) and other volatile and non volatile halides. Due to their high toxicity it is important to control the concentration of these compounds.

TOX is a parameter that is used to estimate the total amount of organic halide present in water. The TOX value is a complex function of several parameters (i.e. pH, Temperature, amount of organic matter and halogen, etc). According to Leo Nollet in the same publication, it is important to remember that TOX may be over estimated because of inorganic halides.

The AOX parameter is comprised within the TOX parameter.

AOX testing is very useful for samples with high levels of solids because in TOX test the columns may block, if, for example, suspended matter is present.

The AOX assay includes a procedure in which carbon is shaken with the sample in flask. Then it is filtered. Both filter and carbon are combusted. The method is sensible to inorganic Chlorine, Bromine, Iodine, but it is not sensitive to Fluorine compounds.

The AOX includes some specific compounds such as AOCL, AOBr and AOI.

This method does not work on concentrations superior to 500 mg/L although concentration of halogenated compounds in water is generally under 100ug/L.

Annex 3 – ISO method for determination of Adsorbable Organically bound Halogens

ISO is the International Organization for Standardization. The norm ISO 9562:2004 concerns water quality and the determination of adsorbable organically bound halogens.

The AOX test is standardized by ISO as described bellow:

"ISO 9562:2004 specifies a method for the direct determination of an amount of usually 10 micrograms per litre in water of organically bound chlorine, bromine and iodine (expressed as chloride) adsorbable on activated carbon.

This method is applicable to test samples with concentrations of inorganic chloride ions of less than 1 g/l. Samples with higher concentrations are diluted prior to analysis. This method is also applicable to samples containing suspended solids where halogens are adsorbed onto the solid matter (e.g. insoluble halides). Filtration of the sample before analysis allows the separate determination of dissolved and particulate adsorbable organically bound halogens (AOX).

Filtered samples with high inorganic chloride content can be analysed by a modified method [dissolved adsorbable organically bound halogens after solid phase extraction in waters with high salt content (SPE-AOX)]. However, results obtained by this modified method can differ significantly from those of the required method." [18]

Annex 4 – Additional information on the parameter chlorine

Definitions:

Total Residual Chlorine (TRC) in wastewater is not a determination of an actual chlorine atom concentration in the way we would determine, for instance, copper concentration. The measure is more of a reactive form of chlorine concentration than anything specific.

TRC is a measure of the **combined available chlorine** and the **free available chlorine** after the demand has been met. While this TRC value can remain the same, the ratio of all the chlorine compounds that make up this value can vary widely.

When chlorine is added to water, some of the chlorine reacts first with organic materials and metals in the water and is not available for disinfection (this is called the **Chlorine demand** of the water.

Free available chlorine is obtained by measuring the total of these three chemical species: Hypochlorous acid (HOCl), hypochlorite ion (OCl^-) and an dissolved gas (Cl_2).

Free available chlorine will also react with ammonia (NH_3) in wastewater to produce chloramines, collectively called **combined available chlorine.**

This way,

Total Residual Chlorine = Total reactive Chlorine

Total Residual Chlorine = Combined available Chlorine + Free Available Chlorine

Hypochlorous acid (HOCl) is a much better disinfectant (by a factor 100) compare to OCl^-, and is often referred to as **active chlorine**.

Chlorine disinfection processes work better at pH lower than 7.3, once HOCl is a more efficient disinfectant compared to OCl^- and at pH lower than 7.3 HOCL is favoured.

Annex 5 – Measuring interferences on the parameter chlorine

Whether you use chlorine gas or sodium hypochlorites to disinfect wastewater, both have one thing in common – in solution they are **reactive** and **very unstable**. The chlorine wants to change from a high oxidizing level to a more stable reduced one. Due to this it is impossible to preserve a sample for residual chlorine. Any sample taken for residual chlorine analysis must be tested immediately.

According to EPA, samples must be tested **within fifteen minutes of collection**. There are also other concerns when sampling for residual chlorine such as exposure to **sunlight** and **sample agitation** reduces the chlorine to ineffective forms.
All of these interferences can be avoided with proper sample collection and handling.

Often, **there may be other interferences that cannot be avoided.** Oxidizing agents such as **bromine** in estuary and marine samples, **oxidized forms of manganese** as well as some other **metals, peroxides, turbidity**, and **color** are often found in wastewaters at levels that will interfere with residual chlorine analyses.

Annex 6 – Full description of the results of the ecotoxicological tests

The following three tables present the detailed results obtained in the ecotoxicological tests:

Table 58 – Full description of the results of the Microtox test

Microtox® *Vibrio fischeri* **(AFNOR NF T90-320)**				**Conditions : T = 15 °C Expositions 5, 15 ou 30 min**			
Sample n°	**Concentration**	**Luminescence (I) à T = 15 min**			**Luminescence (I) à T = 30 min**		
		I_0	I_T	**Lumin (%)**	I_0	I_T	**Lumin (%)**
Control Group		97,9	96,5	100 %	97,9	96,7	100 %
A. Ramsés pH = 8.1	83,3 % 66,7 % 50,0 %	97,2 96,0 97,1	86,7 89,8 94,5	90,6 % 95,1 % 98,7 %	97,2 96,0 97,1	96,2 96,4 102,4	100,3 % 104,0 % 106,6 %
Control Group		97,0	95,4	100 %	97,0	99,6	100 %
B. SF1 Adjusted pH to 8.1	83,3 % 66,7 % 50,0 % 16,7 %	99,3 93,3 95,3 99,2	63,6 70,5 74,2 80,7	64,7 % 76,3 % 78,6 % 82,3 %	99,3 93,3 95,3 99,2	68,7 76,2 78,9 84,3	67,6 % 79,5 % 80,6 % 82,8 %
Conclusions and notes: ***A. "Ramses": No significant effects of acute toxicity*** ***B. "SF1": Slightly toxic (CE_{50} -30m > 100%)*** ***CE_{20} - 30m = 50,1 % [40,8 - 61,6 %]***							

Table 59 – Full description of the results of the *Daphnia magna* test

Daphnia magna ISO 6341													
Sample n°		**Immobilisation - mortality**				**Physico-chemical parameters**							
		A 24 h		**A 48 h**		**T (°C)**		**pH**		**O2 (mg/l)**		**K (µS/cm)**	
Concentration		**N tot**	**%**	**N tot**	**%**	**0 h**	**48 h**	**0 h**	**48 h**	**0 h**	**48 h**	**0 h**	**48 h**
Control Group		0/20	0 %	0/20	0 %		0,21		8,0		8,0		610
A.Ramses pH = 8.1	**100 %** **85 %**	0/20 0/20	0 % 0 %	0/20 0/20	0 % 0 %	[11,4]	19,9	8,1	8,0	9,5	8,0	325	330
B. SF1 **Adjusted pH to 8.1**	**100** **100** **85** **70** **55** **40** **25**	-- 5/20 4/20 2/20 0/20 0/20 0/20	 25 % 20 % 10 % 0 % 0% 0 %	 20/20 20/20 16/20 8/20 0/20 0/20	 100 % 100 % 80 % 40 % 0 % 0 %	[10,8]	 20,0 19,9 19,9	8,8 8,1	 8,6 8,5 8,4	8,2	 8,3 8,1 8,2		 690 680 640
Conclusions – Commentaires: ***A. "Ramses" : No significant effects of acute toxicity*** ***B. SF1: Slightly toxic in 24 hours (CE_{50} -v24h > 100%)*** ***Toxic in 48 hours (CE_{50} -48h = 58,8 % [54,3 - 62,9 %])***													

Table 60 - Full description of the results of the Green Algae test

Green Algue ***Pseudokirchneriella subcapitata (OCDE 201 - USEPA 1003)***		**Organism: *P. subcapitata (S. capricornutum)*** **Microplacs (2ml); 2-3 replicas; 23±2°C; 5 Klux; 0 t/m**		
Sample ***Concentration***		**Algae Growth Density a 72 h (cells/ml)**		
		Mean	**Ecart-type**	**Growth (%)**
Control Group		2.53E+06	8,6 %	100 %
A. "Ramses"	**81,1 %**	2.65E+06	19.6%	104.9%
	57,3 %	3.56E+06	2.6%	141.2%
Filtrated water, with added nutrients	**43,0 %**	4.20E+06	0.7%	166.3%
	28,6 %	4.06E+06	4.3%	160.7%
B'. SF1	***81,1 %***	7.77E+04	1.6%	2.7%
	57,3 %	1.71E+05	19.1%	6.4%
Filtrated water, with added nutrients	***43,0 %***	5.12E+05	26.0%	19.9%
	28,6 %	9.71E+05	10.5%	38.2%
	14,3 %	1.24E+06	5.7%	49.0%
(pH adjusted to 8.1)	***7,73 %***	2.29E+06	1.0%	90.7%

Conclusions – Notes:

A. "Ramses" : No toxic effects (stimulation of the growth)

B. "SF1'' : CE_{50} -72h = 14,2 % [13,5 - 19,5 %]

The inhibition of growth is attributed to the presence of toxic substances

Annex 7 – Discharge Graphics of SF1

This annex present the graphics with the discharges made from SF1 for the times 4 sampling campaigns:

First Campaign (19/06/07):

Figure XXIX - Discharges made from SF1 on the fist campaing (part I)

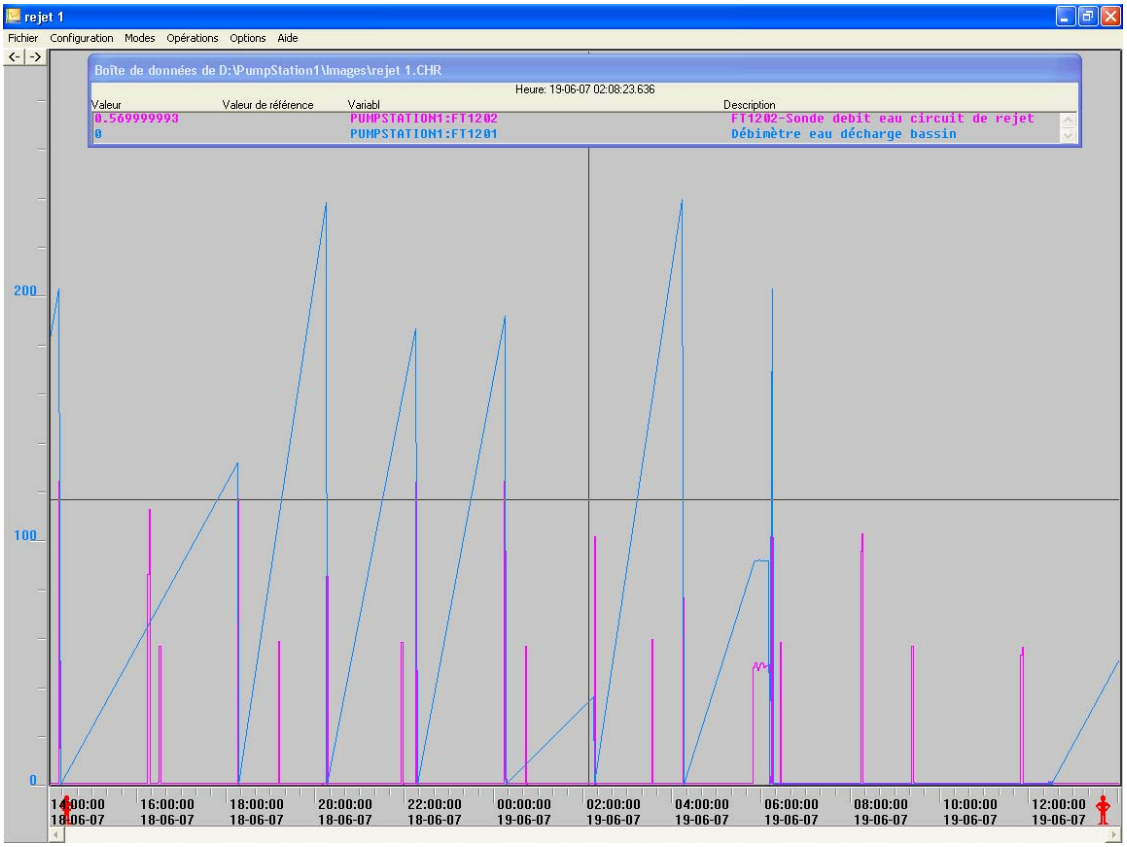


Figure XXX - Discharges made from SF1 on the fist campaign (part II)

Second Campaign (18/09/07):

For the second campaign, there wasn't no digital version of the graphic.
So, although the graphics was utilized it was not possible to present it here.

Third Campaign (18/09/07):

Figure XXXI - Discharges made from SF1 on the third campaign (part II)

Fourth Campaign (18/09/07):

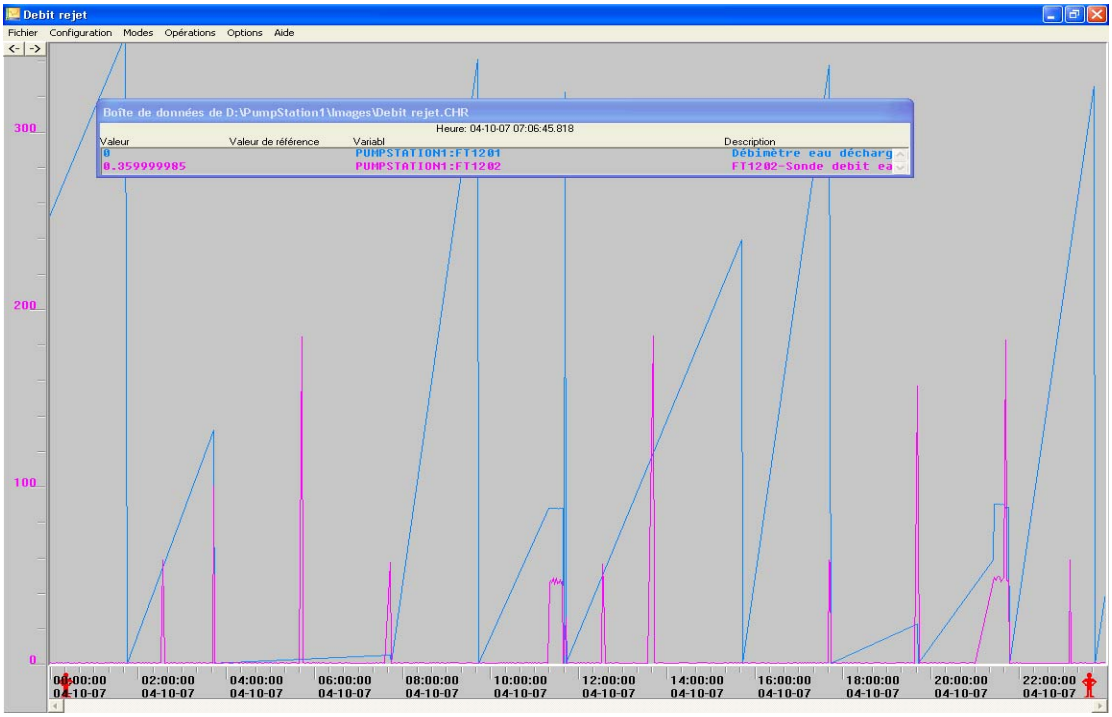


Figure XXXII - Discharges made from SF1 on the fourth campaign (part II)

Annex 8 – Evaluation of the Ecotoxicological Risk

Evaluation of Effects
(Qualification)

Evaluation of the Exposure
(Quantification)

Ecological Potential
PEC / PNEC

Objective:
PEC ≤ PNEC = PEC / PNEC ≤ 1

PEC (Predicted Environment Concentration) = $Q_{effluent} / Q_{receiving\ water\ course}$
PNEC (Predicted No Effect Concentration) = [CE50 ; NOEC] / SF

(where Q is the flow of the river and SF is the Safety Factor)

Example of calculus:

Data on river:
$Q_{effluent}$ = 500 m^3 / day
Q_{river} = 100 m^3 / second = 8.64 x 10^6 m^3 (Average Q_{river})
Q_{river} = 35 m^3 / second = 3.024 x 10^6 m^3 (Minimum Q_{river})

Data on toxicity:

Acute Toxicity (Daphnies + Microtox)	Chronicle Toxicity (Green Algae + Macrophytes)
Average CE_{50} = 12.5%	Average CE_{50} = 3.1%
Average CE_{50} = 2.2%	Average CE_{50} = 0.21%
FS = 1000	FS = 100

PEC = $Q_{effluent} / Q_{river}$

1. Normal Variant:

PEC = 0.0058 %

2 Unfavourable Variant:

PEC = 0.0165 %

Objective is meet

PNEC = [CE50 ; NOEC] / SF

Normal Variant:

Acute Toxicity:	Chronical Toxicity:
PNEC = 0.0125	PNEC = 0.0125
PEC / PNEC = 0.5	PEC / PNEC = 0.2

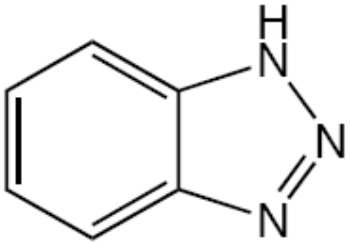
Unfavourable Variant:

Acute Toxicity:	Chronical Toxicity:
PNEC = 0.0022	PNEC = 0.0021
PEC / PNEC = 7.5	PEC / PNEC = 7.9

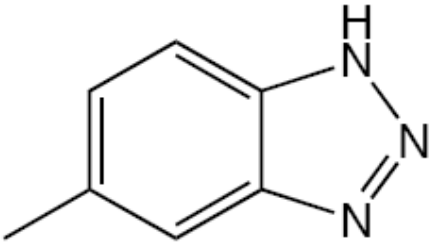
Annex 9 – General data on compounds used in the water treatment of CERN's cooling circuits

Tolyltriazole:

Chemical Formula



Benzotriazole (BT)



Tolyltriazole (TT)

BT and TT are widely used not only as anticorrosive, as CERN does, but also as normal household dishwater detergent. Due to their low biodegradability and limited sorption tendency, BT and TT are only partly removed in wastewater treatment.

The observed environmental occurrences indicate that BT and TT are ubiquitous contaminants in the aquatic environment and that they belong to the most abundant individual water pollutants.

BT and TT are characterized by a high water solubility (28 and 7 g/L, respectively), low vapor pressure, and low octanol water distribution coefficients (log Kow: 1.23 and 1.89, respectively). Because of their application as household detergent additives, these chemicals are very widely used as so-called down-the-drain chemicals, which are discharged in municipal wastewaters. BT and TT are quite resistant to biodegradation. Thus, it must be expected that they widely occur in raw and treated municipal wastewaters and eventually in the receiving, ambient waters. The first reports on the environmental occurrence and on risk assessments of BT and TT were in connection to their application as corrosion inhibitors.

Kolpin et al. detected the anticorrosive TT in 17 of 54 samples from U.S. streams above a reporting level of 0.1 ug/L. The maximum and median values were 2.4 and 0.39 ug/L. These authors did not mention the detection of BT.

Cancilla et al. noticed that a mixture of BT and TT was the primary cause of toxicity to Vibrio fischeri (Microtox). Benzotriazole is classified as toxic to aquatic organisms; it can cause long-term adversary effects in the aquatic environment.

Gigerbt et al state that BT is always more abundant than TT with a BT/TT ratio of 10 to 5. The European BT to TT distribution differs from the findings in the United States, where TT has been found more abundantly.

5-Chloro-2-methyl-4-isothiazoline-3-one:

5-Chloro-2-methyl-4-isothiazoline-3-one is used together with 2-methyl-4-isothiazoline-3-one as an active component in products with trade names such as Kathon CG (1.5%), Kathon WT (15%), Kathon 886 MW (15%) and RH-886 T (56%). In addition to these substances, the products may include water at levels up to 75% and various kinds of salts in varying amounts.

An example is Kathon CG, which contains 1.5% active substance as specified above, 23% magnesium salts and 76.5% water. The substance is used as a preservative in cosmetics and hygiene products and is recommended by suppliers at levels up to 15 ppm in products that are intended to be rinsed off the skin, e.g. shampoo and soap. In products such as mascara, which remain on the skin for a prolonged period of time, recommended levels are 7,5 ppm. Levels of 10-15 ppm are normally used, but in paints levels may be about 30 ppm. Examples of raw materials that may contain Kathon CG are surfactants, polymers (polyacrylates, polycarboxylates) and waxes (wax emulsions)

Effects on environment:

5-Chloro-2-methyl-4-isothiazoline-3-one and 2-methylisothiazoline-3-one are the active components of Kathon CG, among other products. These active components are very toxic to fish and crustaceans (such as Daphnia). Substances that are very toxic are classified as environmentally hazardous. Since Kathon CG contains more than 1% of the active component, it is also environmentally hazardous.

1,3-dichloro-5,5-dimethylhydantoin:

Synonyms:

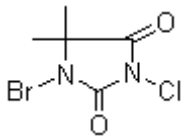
- 1,3-dichloro-5,5-dimethyl-2,4-imidazolidinedione, dichlorodimethylhydantoin,
- dactin,
- daktin,
- dantoin,
- dichlorantin,
- halane,
- hydan,
- omchlor

Main use: antiseptic
Molecular formula: $C_5H_6Cl_2N_2O_2$
CAS No: 118-52-5
EINECS No: 204-258-7
Appearance: white powder
Melting point: 134 - 136 C

Bomo-5,5- Dimethylimidazolidine – 2,4 – dione

Name: 1-Bromo-3-chloro-5,5-dimethylhydantoin
Synonyms: 1-Bromo-3-chloro-5,5-dimethylimidazolidine-2,4-dione

Molecular Structure:



Molecular Formula: $C_5H_6BrClN_2O_2$
Molecular Weight: 241.47
CAS Registry Number: 16079-88-2

Properties: Melting point 158-163°C

Safety Data:

Oxidizing

Corrosive

Risk Codes:

- R8 - Contact with combustible material may cause fire.
- R31 - Contact with acids liberates toxic gas.
- R34 - Causes burns

Zinc chloride:

Zinc Chloride is a chemical coumpound with the formula $ZnCl_2$ and its hydrates. Zinc chlorides, of which at nine crystalline forms are known, are colorless or white and highly soluble in water. $ZnCl_2$ itself is hygroscopic and even deliquescebt.

Zinc chloride possesses wide application in textile processing, metallurgical fluxes and chemical synthesis.

Structure and basic properties:

Four crystalline forms, named polymorphs, of $ZnCl_2$ are known, and in each case the Zn^{2+} ions are tetrahedrally coordinated to four chloride ligands. Rapid cooling of molten $ZnCl_2$ gives a glass, that is, a rigid amorphous solid. Additionally $ZnCl_2$ forms hydrates and at least one mixed hydroxide, ZnClOH.

The covalent character is of the anhydrous material is indicated by its relatively low melting point of 275 °C. Further evidence for covalency is provided by the high solubility of the dichloride in etherial solvents such as wherein it forms adducts with the formula $ZnCl_2L_2$ where L = ligand such as $O(C_2H_5)_2$. Consistent with the Lewis acidity of Zn^{2+}, aqueous solutions of $ZnCl_2$ are acidic solutions: a 6 M aqueous solution has a pH of 1.

Four hydrates of zinc chloride are known. $ZnCl_2(H_2O)_4$ crystallizes from aqueous solutions of zinc chloride. Also characterized are $ZnCl_2(H_2O)_n$ where n = 1, 1.5, 2.5, and 3. When hydrated zinc chloride is heated, one obtains a residue of ZnOHCl.

In aqueous solution, zinc chloride fully dissociated into Zn^{2+}. Thus, although many zinc salts have different formulas and different crystal structures, these salts behave very similarly in aqueous solution. For example, solutions prepared from any of the polymorphs of $ZnCl_2$ as well as other halides (bromide, iodide) and the sulfate can often be used interchangeably for the preparation of other zinc compounds. Illustrative is the preparation of zinc carbonate:

$$ZnCl_2(aq) + Na_2CO_3\ (aq) \rightarrow ZnCO_3\ (s) + 2\ NaCl\ (aq)$$

Safety considerations:

Zinc salts are relatively non-toxic. Precautions that apply to anhydrous $ZnCl_2$ are those applicable to other anhydrous metal halides, i.e. hydrolysis can be exothermic and contact should be avoided. See MSDS in table.

Annex 10 - Complete MSDS of the products used in the water treatment at Building 863 and SF1